

An *ab initio* HCN/HNC Rotational-Vibrational Line List and Opacity Function for Astronomy.

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by

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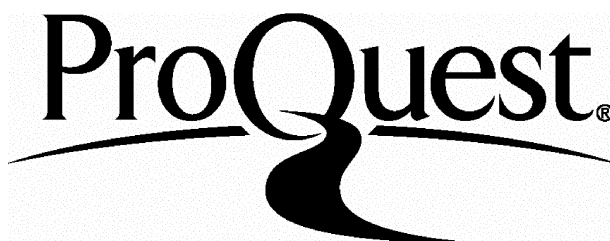
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To my Family.

Abstract

HCN/HNC is an important molecule which is found throughout the universe. For example HCN/HNC is known to exist in comets, planetary atmospheres and the interstellar medium. HCN is also an important opacity source in carbon rich stars (C-stars). HCN masers have been observed in the circumstellar material around these C-stars and also in galaxies. Jørgensen and co-workers investigated model carbon star atmospheres in which they included HCN as an opacity source. They found that including a HCN opacity function had a remarkable effect: the atmosphere expanded by five times and the pressure of the atmosphere in the surface layers dropped by one or two orders of magnitude. This suggests that a full and detailed treatment of the rotational-vibrational spectrum of HCN/HNC could have a profound effect on the models of carbon stars, this provides the main motivation in this work.

The temperatures of the stars in which HCN is an important opacity source $T_{eff} = 2000 - 3000$ K. If HCN and HNC are in thermodynamic equilibrium it would be expected that HNC as well as HCN are found in significant populations. The transition dipoles of the fundamental bands of HNC are more than twice as strong as their HCN counter parts. These factors mean that both HCN and HNC will be considered, which makes a semiglobal treatment of the [H,C,N] system necessary. In this thesis an *ab initio* HCN/HNC linelist, from which accurate spectra and opacity functions can be calculated, is computed.

Within this thesis I present least squares fits for *ab initio* semiglobal potential energy, dipole moment, relativistic correction and adiabatic correction surfaces. The potential energy surface (PES) is morphed for HNC geometries of the potential to improve the HNC representation of the surface.

The PES and dipole moment surface (DMS) are used to perform quantum mechanical nuclear motion (rotational-vibrational) calculations with the DVR3D suite of codes. Preliminary calculations are made to optimise a ro-vibrational basis set and the parameters of the basis functions. Rotational and vibrational energy levels and dipole transition strengths are calculated with various surfaces and are compared with existing experimental and theoretical values. The new PES and DMS are then used to calculate an extensive HCN/HNC linelist containing energy levels, line frequencies and transition dipoles. From

this linelist, room and stellar temperature HCN and HNC spectra are computed and compared with both lab and stellar spectra. Finally, a HCN and HNC opacity function is calculated from the linelist.

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Chapter 1

Astronomical Introduction

The first molecules formed shortly after matter and radiation became decoupled. Since that time molecules have played a very important role throughout the Universe, from the planets through the depths of interplanetary and interstellar space to the stars and galaxies themselves. The importance of molecules on the planet Earth cannot be overstated, for without them there would be no life. The chemistry and spectroscopy of gas phase molecules is a fundamental part of the physics of planetary atmospheres, the interstellar medium and stellar atmospheres.

Following the detection of water in the interstellar medium (ISM) in 1968 [1] there was an explosion in the number of molecules observed in the ISM and a new field of astronomy was born. As of June 2000 the number of molecules that have been observed in the interstellar medium stood at 123 [2]. A further 4 molecules on average are detected per year, this rate shows no signs of slowing down. In the ISM molecules are observed in both emission and absorption. For example from the enigmatic diffuse interstellar bands (DIB) [3] in absorption to maser emission [4] and thermal emission lines [5]. Only molecules that can survive at high temperatures can exist in stellar atmospheres [6]. Consequently only relatively simple high temperature molecules exist and have been observed in stellar atmospheres. The molecules observed in stellar atmospheres as of 1997 [7, 8] are shown in table 1.1. Table 1.1 gives an insight into how the chemistry of stellar atmospheres changes with the C/O ratio.

The increase in atmospheric opacity that accompanies the formation of molecules in stellar atmospheres effects the physics and structure of the stellar atmosphere. In particular polyatomic molecules with their myriad of (10^8) lines have a major effect on the opacity of cool stellar atmospheres that can result in a large back warming effect [6].

Table 1.1: Molecules observed in the atmosphere of cool stars [7]. M-stars are oxygen rich, S-stars have a C/O ratio of unity and C-stars are carbon rich stars, $T_{eff} \sim 4000$ K.

Molecule	Sun	M	S	C	Molecule	Sun	M	S	C	Molecule	Sun	M	S	C
AlH	x	x	x	x	AlO		x			BO		x		
CaH	x	x			CaCl				x	CeO			x	
CrO		x			CrH	x				C ₂	x			
CH	x	x	x	x	CN	x	x	x	x	CO	x	x	x	x
CS				x	CuH	x			x	FeH	x	x	x	
GeH				x	H ₂	x	x	x	x	HF	x	x	x	x
HCl	x		x		LaO			x		MgH	x	x	x	
MgO		x			NH	x	x		x	NiH	x			
OH	x	x	x		ScO	x	x	x		SiF		x		
SiH	x	x	x	x	SiN		x			SiO	x	x	x	
SnH				x	TiH	x	x			TiO	x	x	x	
TiS			x		VO		x	x		YO		x	x	
YS			x		ZnH				x	ZrO	x	x	x	
ZrS			x		SiH ⁺	x				CH ⁺	x			
C ₂ H				x	C ₂ H ₂				x	C ₃				x
CaOH		x			HCN				x	H ₂ O	x	x		
SiC ₂				x										

This backwarming effect, assuming hydrostatic equilibrium, will result in an atmospheric structure that is different than would otherwise be expected.

This thesis deals with just two of the 123+ molecules detected in the interstellar medium. These are the isomer pair of HCN and HNC.

1.1 HCN and HNC in the Universe.

HCN and HNC are extremely important molecules throughout the universe. For example HCN has been observed in galaxies [9, 10], comets [11, 12], planetary atmospheres [13], molecular clouds [14, 15], carbon star atmospheres [16, 17] and circumstellar masers [18]. Conversely, prior to its detection in the interstellar medium in 1971 by the radio

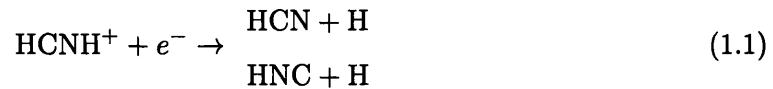
astronomers Snyder and Buhl [19, 20], HNC had only been observed in the laboratory by means of matrix isolation spectroscopy.

1.1.1 Molecular Clouds and YSO's

Hydrogen cyanide is one of the most important interstellar molecules and has been observed in both Galactic and extra-galactic [21] objects. Similarly HNC is also observed in many molecular clouds. Importantly the large electric dipole moment of HCN of 2.985 D [22] make the critical density of the $J = 1 \rightarrow 0$ transition high. This makes HCN a good tracer for dense molecular regions.

An interesting phenomenon in the ISM is the high HNC/HCN abundance ratio. The temperature of the ISM where HCN and HNC are found is of the order of 10-100 K. From the latest *ab initio* calculations [23] (see chapter 5) HNC lies 5185.6 cm^{-1} above the HCN zero point energy (ZPE). At thermodynamic equilibrium at $T < 100$ K one would expect the HNC/HCN ratio to be about 10^{-33} . Earlier estimations [15], which used an inferior value of the relative energy of the HNC ground state, gave a HNC/HCN ratio of 10^{-25} . If HNC and HCN are in thermodynamic equilibrium HNC should not be detectable in the ISM. However, HNC has been detected in the ISM and in some cases the HNC/HCN ratio has been observed to be greater than unity. For example Hirota *et al* [15], observed the HNC/HCN ratio to be 4.5 ± 1.2 in L1498, a dark molecular cloud. The reason for this high abundance ratio must lie in the height of the barrier to isomerisation and the preferential formation of HNC. Once HNC has formed there is simply not enough thermal energy at 100 K to overcome the isomerisation barrier at $\sim 16000 \text{ cm}^{-1}$ and allow the isomerisation of the molecule. So once formed in the ISM, HNC will persist for long periods of time.

Two dissociative recombination reactions have been suggested as the formation route for HNC, the first by Herbst [24]:

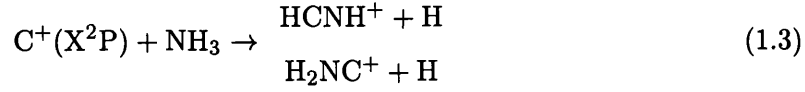


This reaction has an almost equal branching ratio. This second reaction was proposed by Allen *et al* [25]:



Clearly a combination of reactions 1.1 and 1.2 would produce a ratio of HNC/HCN that is greater than one. Reactions leading to the production of the parent molecules of

reactions 1.1 and 1.2 have been studied using quantum chemical techniques by Talbi and Herbst [26]. The particular generation process studied was:

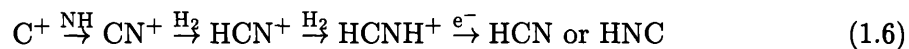


However they found that the residual internal energy of the molecule after the reaction was sufficient to overcome the isomerisation barrier. Consequently 98% of the reaction product is HCNH^+ and H_2NC^+ is a minor product. Further to this work Herbst *et al* [27] studied the 2 other possible reactions to generate HCN and HNC this time with neutrals:



Herbst *et al* again found that in both cases the remaining internal energy was more than enough to overcome the isomerisation barrier. As a result they found that both reactions produce HCN and HNC in near equal abundance. Although the reason for the thermodynamic disequilibrium of HNC/HCN ratio in molecular clouds appears clear, the mechanism of production of HNC is still not fully understood.

HCN has also been observed in post asymptotic giant branch (AGB) objects [28], otherwise known as proto-planetary nebulae (PPNe) and also in cool (25 K) clumps in evolved planetary nebulae (PNe) [29]. It is believed that as a PNe evolves from PPNe to an evolved PNe the abundances of SiO, SiC₂, CS and HC₃N decrease and the abundances of CN, HCN, HNC and HCO⁺ increase. The average HNC/HCN ratio of 0.6 in PNe is similar to the ratio's seen in the ISM. However, the conditions inside a PNe are vastly different to the conditions in a molecular cloud in the ISM. Firstly the central star provides an ultraviolet (UV) flux that is orders of magnitude stronger than in the ISM. Secondly strong stellar winds from the central star may generate violent shocks within the nebula. As a result of these extreme conditions the chemical composition and chemistry of PNe are different to that of the ISM. Ali *et al* [30] have modeled the PNe NGC 6781, M4-9 and NGC 7293. The abundances of HCN and HNC in their models are in good agreement with experiment. The formation routes for HCN and HNC used by Ali *et al* were:



These HCN and HNC generating reactions are clearly different from the proposed reaction routes in molecular clouds.

The preceding discussions have involved objects that are cold. In those regions HCN is detected primarily by rotational microwave emission. There are hotter (up to 1000 K) regions of the ISM in which HCN has been observed. For example Lahuis and van Dishoeck [31] have taken infrared spectra of gas towards several deeply embedded massive young stellar objects (YSO's). Their observations were performed with the short wavelength spectrometer (SWS) on the infrared space observatory (ISO) satellite. Figure 1.1 shows the final spectra taken, towards 12 YSO's, by Lahuis and van Dishoeck. Clearly visible in most of these spectra is the HCN v_2 bending fundamental and one of the $v_2 = 1 \rightarrow 2$ hot bands is visible in several of the spectra. The temperature of the HCN in these objects was determined to be between 300 and 1000 K. The hot bands present in the spectrum indicate that higher vibrational levels are significantly populated. This means that to accurately model these objects spectroscopic data on the higher lying vibrational modes is needed.

HCN and HNC are endemic to the ISM, and are present in many types of object and over a large range of temperatures. However, HCN and HNC are not only seen in the ISM.

1.1.2 Comets

Cometary HCN was first observed by Huebner *et al* [11] in 1974. Since then HCN has been observed in many comets and HNC has been recently observed in comets Hyakutake [12], Hale-Bop [32], Lee [33] and 1999 S4 (LINEAR) [34]. In each case the HCN/HNC ratio has been measured and been found to be comparable to that observed in molecular clouds. This raises the question why is the HCN/HNC ratio so high in the coma of comets? Does the HCN and HNC in the coma come directly from the nucleus. If so are the HCN and HNC molecules primordial, a relic of the Solar nebula from which the sun and solar system formed. Biver *et al* [32] found the HNC/HCN ratio increased with decreasing Sun-Comet distance, from 2% at 2.9 AU to 20% at 1.4 AU. If HNC is a component of the nucleus it would be expected that the HCN/HNC ratio be constant. Four possible explanations were proposed:

1. HNC is a parent species, it is destroyed in reactions.
2. Gas phase chemical reactions convert HCN to HNC.

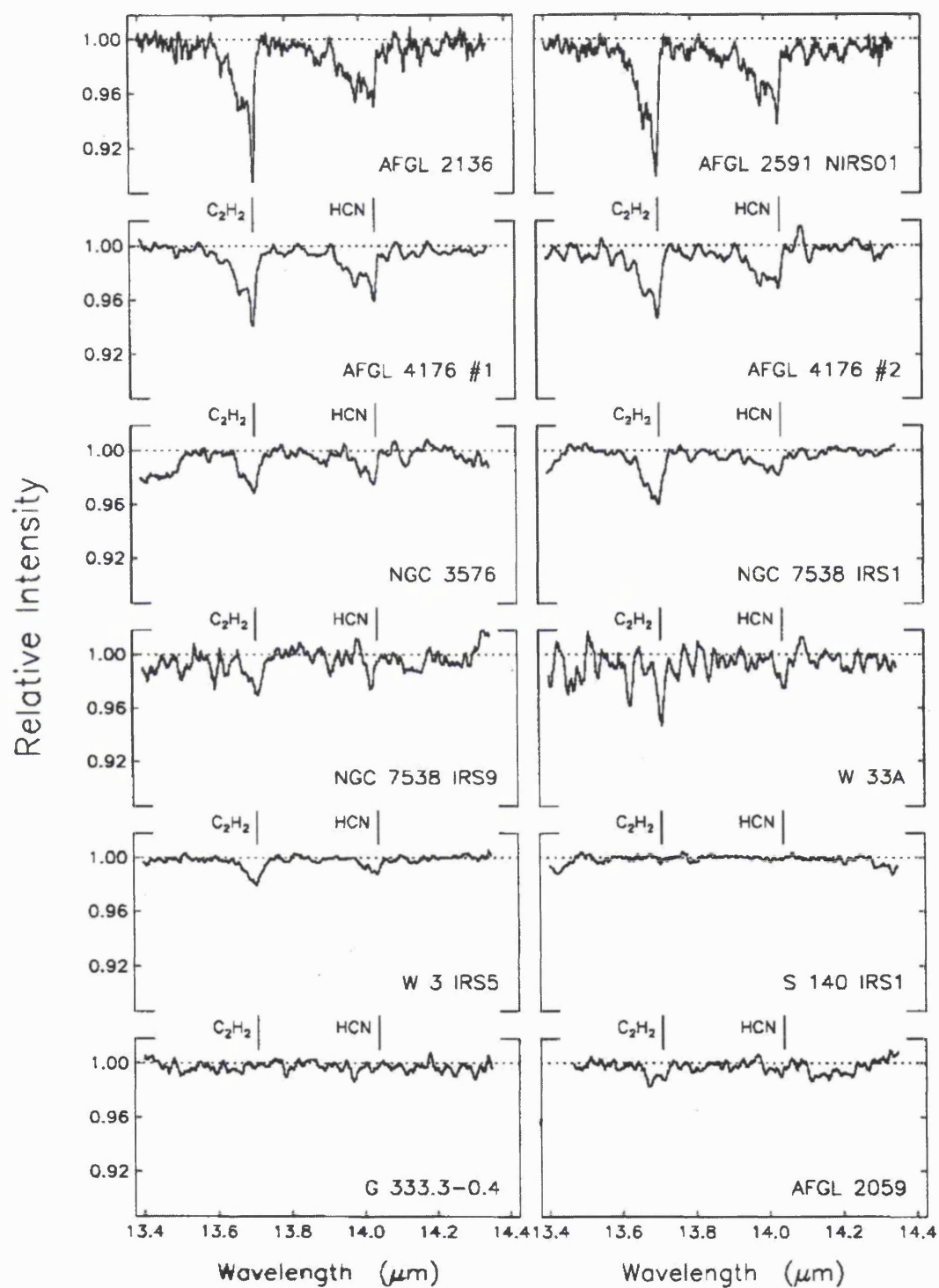


Figure 1.1: ISO SWS spectra taken towards 12 YSO's. The HCN bending mode is indicated.

Figure taken from Lahuis and van Dishoeck [31].

3. Photoexcited HCN decays to HNC.
4. HNC is produced via photodissociation of larger molecules.

The very high excitation energy required to overcome the isomerisation barrier of HCN, makes option 3 very unlikely. Rodgers and Charnley [35] performed hydrodynamical-chemical modeling of cometary comae. They concluded that the chemically induced isomerisation of HCN to HNC via reaction with suprathermal H atoms was the most likely source of HNC. Recently with the benefit of more observational data, primarily that of comet Lee, Rodgers and Charnley [36] repeated their modeling. This time they concluded that

1. Ion-Molecule chemistry is unable to produce the observed levels of HNC by more than an order of magnitude.
2. Isomerisation of HCN by energetic H atoms fails to generate sufficient HNC atoms for comets Lee and Hyakutake.
3. Photo-fragmentation of unidentified large molecules is a viable formation route of HNC.

Point 2 conflicts with their earlier findings and point 3 is rather vague. There is also the possibility that their initial conditions are incorrect. The debate on the origin of cometary HNC is still open.

1.1.3 Planetary Atmospheres

HCN was first observed in the atmosphere of the gas giants by the Voyager 1 space probe. Since then HCN has been observed in the atmospheres of many of the outer planets. This includes Neptune [37], Jupiter [38], Saturn and Saturn's moon Titan [39]. Weisstein and Serabyn [40] have put the mole fraction of HCN between 0.3-2 parts per billion (ppb) in Jupiter's atmosphere and 0.2-15 ppb in Saturn. The large uncertainty in their values for the mole fraction of HCN is a result of uncertainties in the amount of HCN condensation. Weisstein and Serabyn attributed these uncertainties to the sensitivity of HCN vapor pressure to temperature near its saturation point. Marten *et al* [37] observed HCN in the stratosphere of Neptune with a mole fraction of 1 ppb. They believed HCN to have condensed out in the troposphere. No HNC has been observed in the atmospheres of the giant planets. However Petrie [41] has made an attempt to model the chemistry of the

ionosphere of Titan to estimate the concentration of HNC, to assess the possibility of it being detected by the forthcoming Cassini-Huygens mission. In Petrie's models HNC is generated in the ionosphere by the same dissociative recombination reaction (reaction 1.1) that is believed to generate HNC in interstellar clouds. However HCNH^+ has not been observed in Titan's atmosphere which is $\sim 97\%$ N_2 , with a high abundance of methane and Argon. Many reactions in the upper atmosphere of Titan are driven by solar photons and electrons and thus may lead to the generation of HNC. Petrie, in his model, included various reactions in which HNC is destroyed. For example protonation to form HCNH^+ , H driven isomerisation and reactions with other radicals. Petrie concluded that the peak concentration of HNC was likely to be $10^4 - 10^5$ molecules cm^{-3} . This small amount of HNC is unlikely to be detected by the Cassini probe. However, Petrie concluded that HNC is an important trace species in the ionosphere and that many products of HNC reactions may be detectable.

1.1.4 Carbon Star Atmospheres and Circumstellar Material.

HCN has been observed to be one of the most abundant molecules in the atmospheres of carbon stars (C-stars) with $T_{\text{eff}} < 2800$ K. HCN has also been observed in the sub-millimeter in circumstellar envelopes (CSE) (for example [17]) and masers around C-stars [42, 43]. Many HCN maser lines have been detected since the first HCN maser line (02^0_0) $J = 0 - 1$) was observed in IRC+10216 by Lucas *et al* [42]. These maser lines have been observed in the HCN ground state and excited vibrational bending modes (01^1_0), (02^0_0) and (04^0_0). Dinh-V-Trung and Nguyen-Q-Rieu [44] have modelled the rotational transition $J = 0 - 1$ in several vibrationally excited states. Their results suggest that the absorption of infrared photons could cause a population inversion in the $J = 1 - 0$ transition in the excited C-H stretch mode (10^0_0).

Of particular interest to us is the role of HCN in the opacity of C-star atmospheres. Secchi [45] in 1868 first noted the peculiar spectrum of C-stars and classified them as "class four". In the near infrared Querci and Querci [46] in 1970, identified lines from HCN bands in the spectrum of the C-star UU Aur. The bands that they claimed to identify were the (40^0_0) overtone the (30^0_1) and (20^0_3) combination bands and the (01^1_0) $\rightarrow$ (41^1_0) hot band. At one micron Giguere [47] tentatively identified the (30^0_0) overtone band in the carbon stars UU Aur. Johnson and Mendez [48] observed a $3 \mu\text{m}$ absorption feature in 7 carbon star spectra which were taken using a Mertz-type Michelson interferometer. Fay

and Ridgeway [49], via narrow band filter photometry, observed 23 stars and also found a $3.2\ \mu\text{m}$ absorption feature which they noted corresponds to the wavelength of the C-H stretch mode common to hydrocarbons. Later Noguchi *et al* [50] observed a $3\ \mu\text{m}$ absorption feature in a further 22 Carbon stars that was not present in the 23 M-type stars that they surveyed. Finally in 1978, Ridgeway *et al* [51] identified the cause of the $3\ \mu\text{m}$ feature as the C-H stretch mode of HCN and C_2H_2 . The spectra of stars at longer infrared (IR) wavelengths cannot be measured from the ground due to molecular atmospheric absorption. As a result the observation of the HCN bending mode had to wait until the launch of the infrared satellites.

The first of the infrared satellites was the infrared astronomical satellite (IRAS) which began and ended its 10 month mission in 1983. IRAS was primarily an all sky infrared survey mission. Consequently the low resolution spectrometer (LRS) on board IRAS had a relatively low spectral resolution (20-60) and covered wavelengths of 8 to $23\ \mu\text{m}$. More detailed mid to far IR spectra became available with the the infrared space observatory (ISO) launched in 1995. The short wavelength spectrometer (SWS) on board ISO, made the entire spectral range from 2.5 to $45\ \mu\text{m}$ available. Many workers have used ISO to take spectra of carbon stars in this wavelength range. For example, Aoki *et al* [16, 52] have measured spectra in the regions $3\text{-}8\ \mu\text{m}$ and $8\text{-}20\ \mu\text{m}$. Figure 7.10 shows the spectrum of 6 carbon stars in the range $3\text{-}8\ \mu\text{m}$ from Aoki *et al* [16] which were taken with the ISO SWS. Clearly visible in the spectrum is the $3\ \mu\text{m}$ absorption feature. The authors have also marked other bands of HCN, including the (02^00) bending overtone. Figure 1.2 shows the spectra of 4 carbon stars in the region $8\text{-}20\ \mu\text{m}$ from Aoki *et al* [52] which were taken with the ISO SWS. Clearly visible is a $14\ \mu\text{m}$ feature which corresponds to the HCN bending fundamental mode. The solid lines in the spectra are Planck functions fitted to the spectra.

These spectra indicate that HCN is a major source of opacity in the atmospheres of C-stars.

How far does the influence of HCN and possibly HNC extend? Eriksson *et al* [53] were first to attempt to include a HCN opacity function in their model atmospheres. Prior to this work models such as those of Johnson [48] who included HCN in chemical equilibrium calculations only. Eriksson *et al* [53] calculated model atmospheres which include opacities of CO, CN, C_2 and C_2H_2 , both with and without a HCN opacity function. Figure 1.3 shows temperature verses logarithmic gas pressure for model atmospheres with

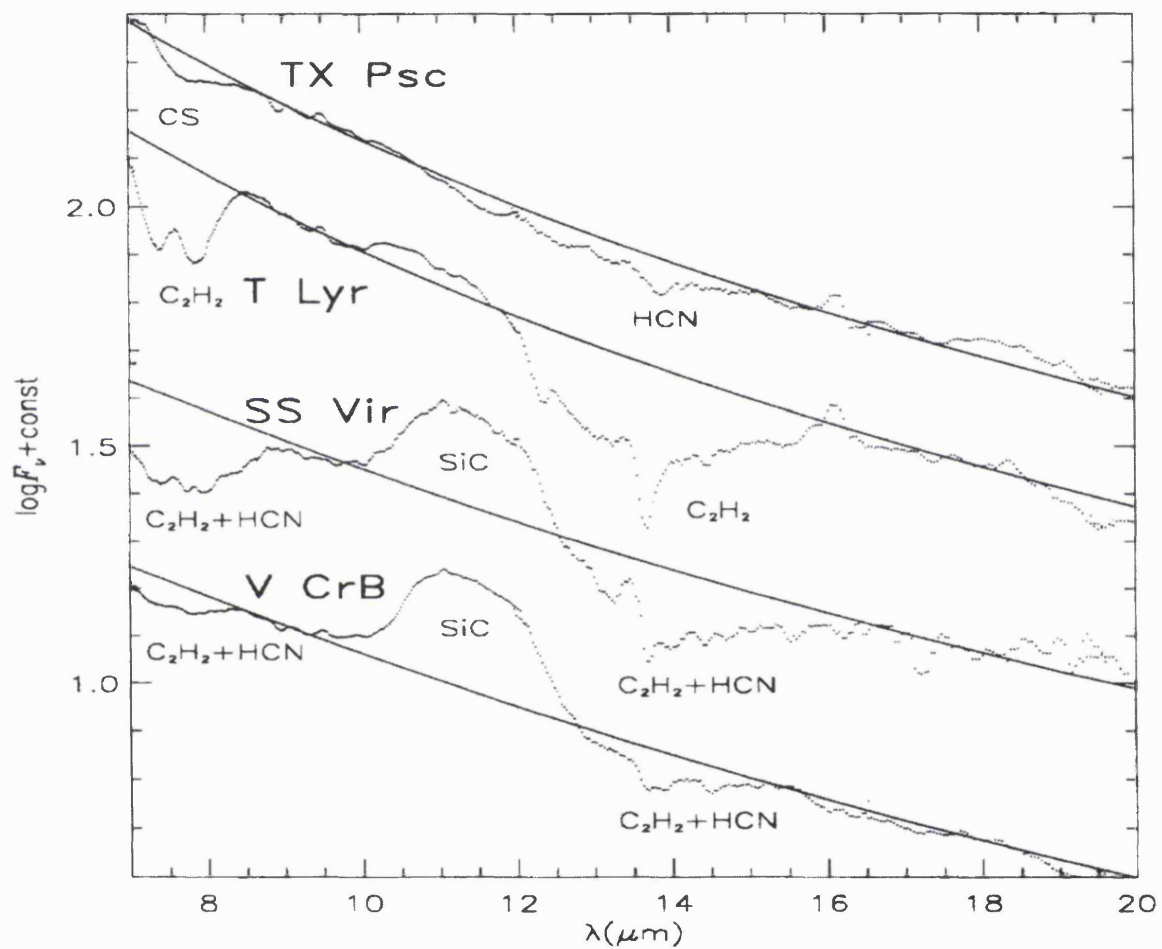


Figure 1.2: ISO SWS spectra of 4 carbon stars in the region 8-20 μm . Taken from Aoki *et al* [52], solid lines are Planck functions fitted to the spectra.

various T_{eff} . There is a huge difference between upper atmospheric pressure of the model atmospheres with $T_{eff} = 2900$ and 2800 K. In these models there is a high CN abundance at $T_{eff} = 2900$ K, and consequently a high CN opacity. As the temperature decreases CN becomes depleted by the formation of HCN, and the model atmosphere without HCN opacity becomes more transparent. This results in the drop of atmospheric pressure and contraction of the atmosphere. When Eriksson *et al* included a HCN opacity function the total opacity in the outer layers of the cooler atmospheres ($T_{eff} = 2800$ K) was increased dramatically and the gas pressure was increased. The HCN opacity function used by Eriksson *et al* was based on a crude empirical estimate of the intensities of the combination bands of HCN. At the time Eriksson *et al* were undertaking their work the intensity of only the fundamental bands of HCN was known. The intensities of the combination bands were estimated by assuming the ratios of the transition probabilities of the fundamental bands to the combination bands behave in a similar fashion to those of more well studied molecules. The work of Eriksson *et al* [53] served to demonstrate the importance of HCN opacity in C-star atmospheres and the need for more HCN spectroscopic data.

As a follow up work Jørgensen *et al* [54] performed *ab initio* complete active space self consistent field (CASSCF) and contacted configuration interaction (CCI) calculations on HCN bands below $10\,000\text{ cm}^{-1}$. The resulting data were then included in their model atmospheres. Figure 1.4 shows the logarithmic pressure verses atmospheric height for model atmospheres of Jørgensen *et al* [54] at $T_{eff} = 2500$ K. The line with triangles represents the atmosphere without an HCN opacity. Clearly figure 1.4 there is a massive difference between the atmospheres with and without HCN opacity. Jørgensen *et al* [54] went on to say:

“Accounting for HCN opacity causes the atmosphere to expand by a factor of 5 and lowers the gas pressure by one or two orders of magnitude.”

Figure 1.4 also highlights the importance of the HCN opacity data used. For example there is a clear difference between model atmosphere HCN opacity calculated with the CCI approximation (+ symbols) and HCN opacity calculated with the CASSCF approximation (filled box symbols). The calculations of Jørgensen *et al* considered vibrational motion only. Therefore the interaction between rotation and vibration was not taken into account. Jørgensen *et al* [54] made approximations to account for the degeneracy of the v_2 mode. Furthermore Jørgensen *et al* [54] calculated only the HCN levels less than $10\,000\text{ cm}^{-1}$ and neglected HNC. The opacity data of Jørgensen *et al* [54], has recently been used by

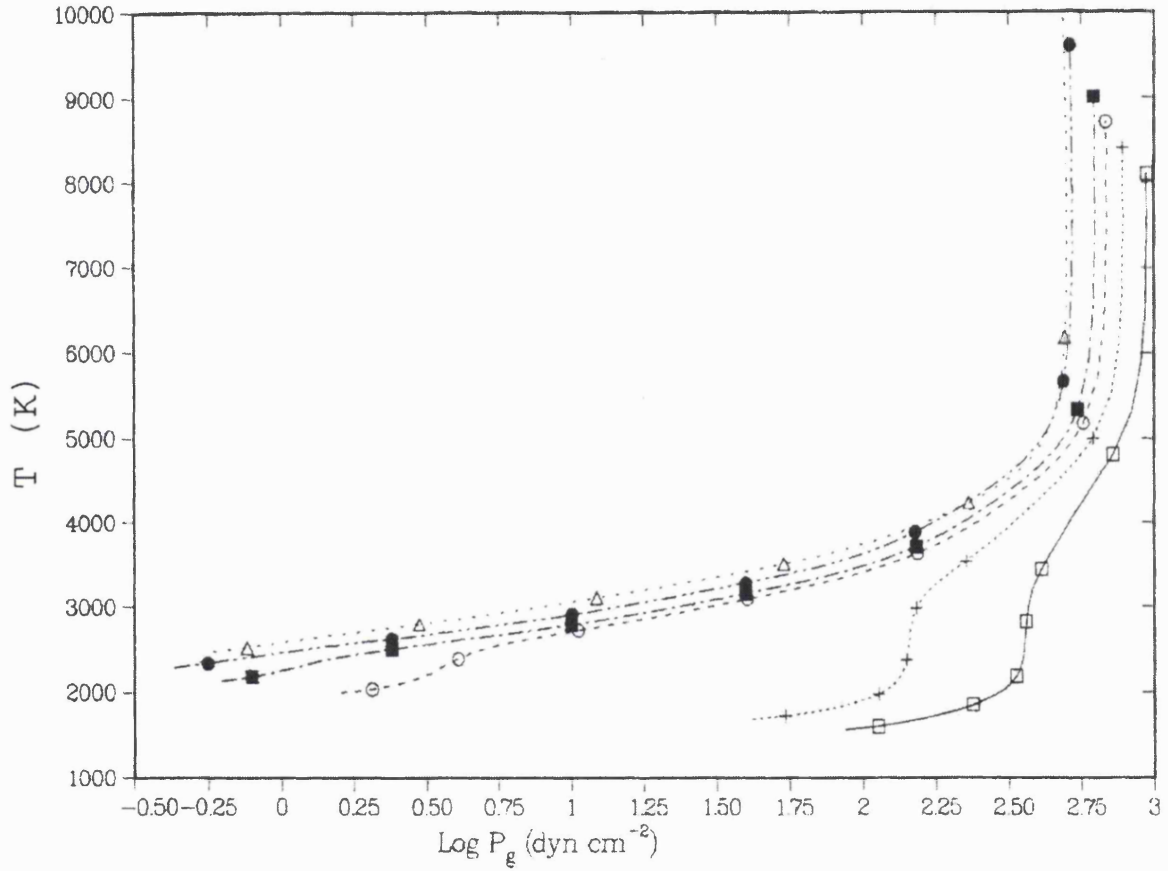


Figure 1.3: Temperature versus logarithmic gas pressure for carbon star model atmospheres of Eriksson *et al* [53], without HCN opacity. Curves from right to left are $T_{eff} = 3500, 3200, 3000, 2900, 2800$ and 2700 K. Symbols are positioned at optical depths of $10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, 10$ and 10^2 . Figure taken from Eriksson *et al* [53].

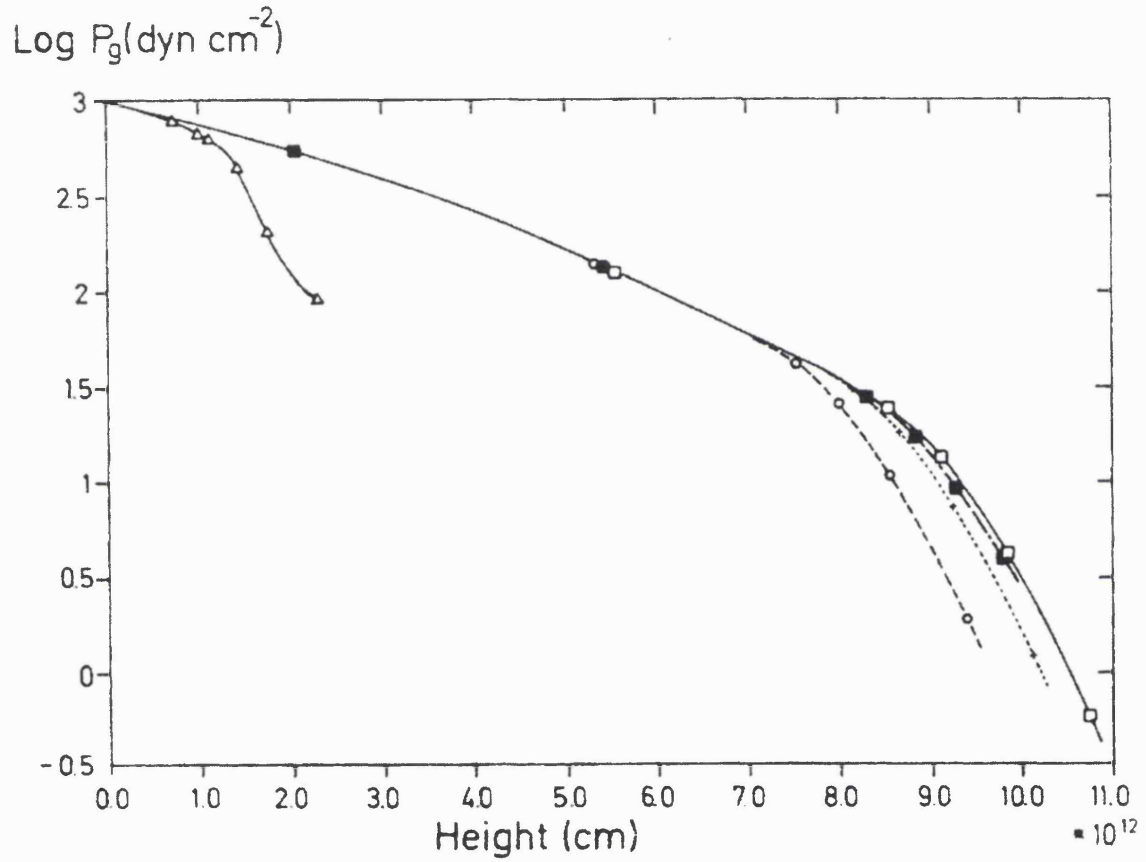


Figure 1.4: Logarithmic pressure verses atmospheric height, for the C-star model atmospheres of Jørgensen *et al* [54] at $T_{eff} = 2500$ K. The curve marked with $\triangle$ symbols represent the model atmosphere without HCN opacity, the other curves are model atmospheres with some form of HCN opacity. Again symbols are placed at optical depths of 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} , 10 and 10^2 . Figure taken from Jørgensen *et al* [54].

Loidl *et al* [55] in their C-star model atmospheres. Whilst recently others such as Aoki *et al* [16] have used HCN opacities based on the available HCN experimental data. However neither source of data is full enough to cover all the bands that will contribute to the full HCN opacity and both neglect HNC. The *ab initio* data of Jørgensen is also inaccurate by today's standards.

The work of Eriksson *et al* and Jørgensen *et al* [53, 54] suggest that the proper detailed treatment of the vibration-rotation spectrum of HCN can have profound effect on the structure of the C-star model atmospheres. It is this problem that motivated this thesis and the project to calculate an extensive rovibrational linelist up to high levels of rotational excitation. This linelist will greatly extend the HCN and HNC data available at high energies and thus enable the construction of a more accurate high temperature HCN/HNC opacity function.

1.2 Carbon Stars.

In the previous section the importance of HCN in carbon star atmospheres was discussed, but what is a C-star? Prior to 1977 all C-stars were thought to be exclusively asymptotic giant branch stars (AGB) [56]. However in 1977 Dahn *et al* [57] discovered the first dwarf carbon star (dC-star). Little is known about dC-stars, due to their rareness and low luminosity. Dwarf carbon stars are unusual stars, they are thought to be formed by mass transfer from a companion star that is now a white dwarf. Dearbone *et al* have performed a detailed study of the dC-star G77-61. The effective temperature of this star is 4100 K, a late k-dwarf. It lies below the main sequence as a result of extreme metal deficiency. It has a companion white dwarf and a mass of $\sim 0.35 M_{\odot}$. The discussion of carbon stars, from here on, will focus on the well studied giant C-stars.

AGB C-stars, due to their high luminosity, are the most heavily studied and observed carbon stars. An AGB star is a medium to low mass star ($\sim 1 < M < 10 M_{\odot}$ [56]) that is in the final throws of its life. Eventually the sun will become an AGB star. AGB stars as their name suggests are giant in size, having a typical radius of ~ 3 AU and they have strong stellar winds with typical $\dot{M} = 10^{-7} M_{\odot} \text{ yr}^{-1}$ and up to $\dot{M} = 10^{-5} M_{\odot} \text{ yr}^{-1}$ [56]. These stars are relatively cool, resulting in their red colouring, but highly luminous.

To aid the description of the structure of an AGB star I will give a very brief description of the evolution of a population I, solar mass star, for a more detailed discussion see refs [58, 59]. Figure 1.5 shows the evolutionary path of a population I, solar mass star on the

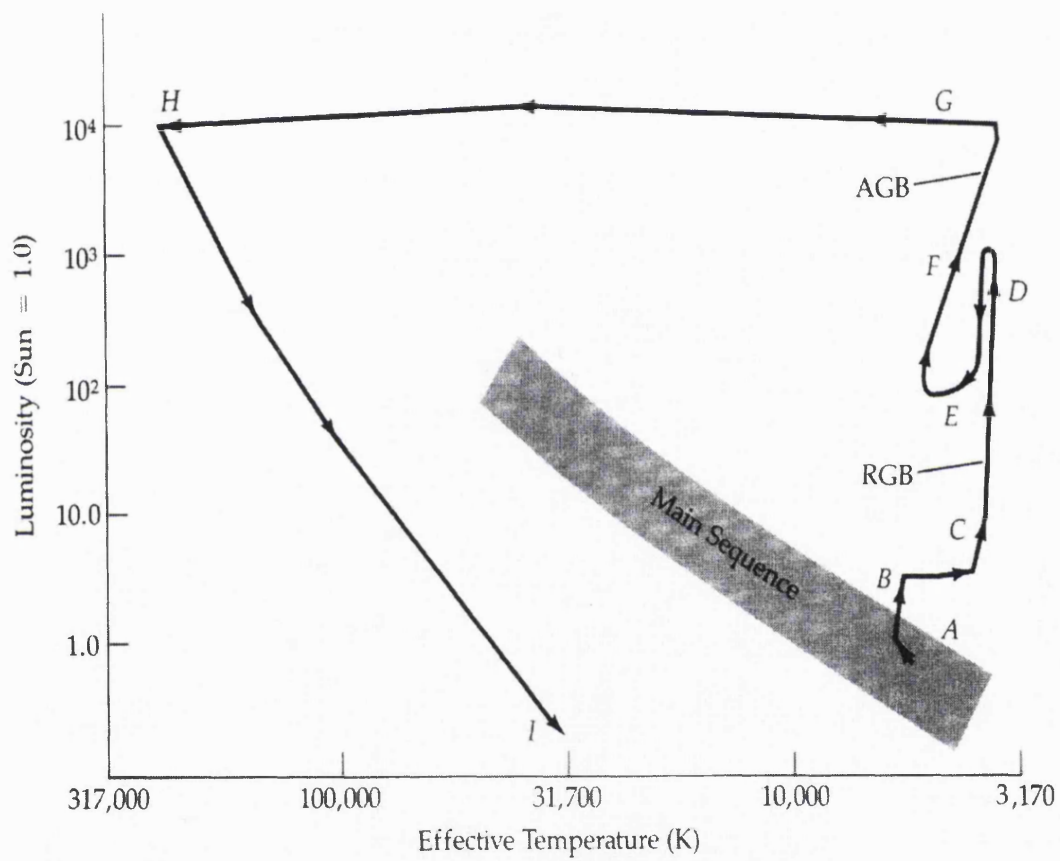


Figure 1.5: The evolutionary path of a solar mass star of population I. Figure taken from Zeilik *et al* [58].

H-R diagram. From points A to B the star is in the main sequence, H fusion in the core generates the energy.

After about 10^{10} years, the H fuel for fusion in the core has been exhausted and fusion in the core stops. H fusion continues in a shell around the inert He core, the He core shrinks, heats up and becomes degenerate. The increase in core temperature causes the star to expand cool, points B to C. As the atmosphere cools it becomes opaque and heat transport becomes dominated by convection. At this point the star becomes increasingly luminous and climbs the red giant branch (RGB), points C-D.

Meanwhile the core has been contracting and heating up. Eventually the core temperature reaches $\sim 10^8$ K and He fueled fusion reactions start. This causes a surge in temperature which spreads rapidly through the degenerate core igniting more He fusion reactions and heating the core further. This temperature runaway is the Helium flash, at the peak between points D and E. The temperature continues to increase until it reaches $\sim 4 \times 10^8$ K. At this point the core becomes non-degenerate, expands and cools. He burning proceeds in the core and the envelope contracts and warms up and the star luminosity drops. The He core burning phase, point E, is analogous to the H core burning phase on the main sequence.

Eventually the He is exhausted in the core and fusion ceases in the core. He burning in a shell around the core continues. In a similar fashion to the red giant phase, the He shell burning causes the atmosphere to expand and cool, point F. H shell burning starts further out, and begins to dominate energy production. The star continues to expand and cool, asymptotically approaching the RGB, this is the asymptotic giant branch (AGB). The He shell burning is highly sensitive to temperature increases. If the star contracts slightly the slight increase in temperature can cause the He burning to flare up. This causes the temperature to dramatically increase and the stars atmosphere to expand, cool and then shrink again. The process is repeated and the star pulsates. These thermally driven pulsations make AGB stars unstable. Some of the product of the flare up in He shell burning are thrown up and carried by convective processes to the upper atmosphere. This is often called the third dredge up which enriches the atmosphere with heavier elements such as C, N and O.

Towards the end of the AGB phase the star develops a very strong wind called a super-wind. As a result of this mass loss many AGB stars are surrounded by extensive circumstellar material. Eventually the wind becomes so strong that the atmosphere is

blown off leaving behind a hot core and an expanding envelope of gas which is heated by the hot core. This is the white dwarf and planetary nebula end phase.

The atmosphere of an AGB star is enriched with the products of He fusion. In the case of a C-star the C/O ratio is greater than unity. It is this enrichment that results in the rich chemistry of C-stars. The observed C/H, N/H and $^{12}\text{C}/^{13}\text{C}$ ratios in C-stars are close to solar abundance suggesting that much of the C and N in the Galaxy originated in these stars [56]. The chemistry of C-star atmospheres is dependent upon the elemental abundances (such as the C/O ratio) and the effective temperature of the atmosphere. For example see ref. [16]. At $T_{eff} = 2500$ K HCN is a major opacity source, at higher temperature CN becomes more important due to its higher abundance. At lower temperatures C_2H_2 may become a more important opacity source and at yet lower temperatures dust, graphite and silicon carbide may effect atmospheric structure [54]. The modeling of stars is made more complex by the variable nature of AGB stars [55]. For example Jørgensen *et al* [60] commented that the T_{eff} of TX Psc had changed by 100 K between three separate observations over 16 years. However the limitations of the measurement of effective temperature usually result in errors that are greater than 100 K. This makes it unlikely that a temperature change of 100 K can be reliably measured over a 16 year period.

1.3 Some Basic Concepts of Stellar Atmospheres.

In this section, I will discuss some of the basics concepts of stellar atmospheres and atmosphere modeling.

The **luminosity** (L) of a star is defined as the total amount of radiation leaving the stellar surface per unit time.

The **effective temperature** (T_{eff}) of a star is defined as the temperature a black body would need to radiate the same energy as the star per unit area. T_{eff} can be related to the stars luminosity:

$$L = 4\pi R^2 \sigma T_{eff}^4 \quad (1.7)$$

Where σ is the Stefan-Boltzmann constant and R is the stars radius. For most stars the radius or angular diameter is not known so determining the effective temperature is not as straight forward as equation 1.7. It is therefore usual to fit a model atmosphere to

the observed stellar spectrum, to determine the effective temperature. This is the method used by Aoki *et al* [16] and Jørgensen *et al* [60].

Intensity (I_ν) in astrophysics terms is the amount of energy passing through the area dA into a solid angle $d\omega$ per unit frequency ($d\nu$) per unit time. If E_ν is the energy radiated per unit time at frequency ν , then:

$$I_\nu = \frac{E_\nu}{d\omega dA d\nu} \quad (1.8)$$

Consider a beam of radiation passing through a volume of gas. As the radiation passes through the gas the gas absorbs some of the radiative energy. The energy per unit time moving across the distance ds is reduced by:

$$dE_\nu = -\kappa_\nu \frac{E_\nu}{dt} ds = -\kappa_\nu I_\nu d\omega d\nu dA \quad (1.9)$$

Where κ_ν is called the absorption coefficient and is a function of frequency. At this point the **optical depth** (τ_ν), which is a function of frequency, can be introduced. Where $d\tau_\nu = \kappa_\nu ds$ and:

$$\tau_\nu(s) = \int_0^s \kappa_\nu ds \quad (1.10)$$

In a similar fashion to absorption the gas will emit radiation and increase the energy in the beam. The energy per unit time is increased by:

$$dE_\nu = \varepsilon_\nu d\omega d\nu ds dA \quad (1.11)$$

Where ε_ν is the amount of energy emitted per unit time per unit volume per unit solid angle per frequency band and is a function of ν . Combining equations 1.11 and 1.9 we arrive at:

$$dE_\nu = -\kappa_\nu I_\nu ds d\omega d\nu dA + \varepsilon_\nu ds d\omega d\nu dA \quad (1.12)$$

By using the definition of I_ν (equation 1.8) we have:

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + \varepsilon_\nu \quad (1.13)$$

By dividing through by κ_ν and using the definition of $d\tau_\nu$ we obtain:

$$\begin{aligned}
\frac{dI_\nu}{d\tau_\nu} &= -I_\nu + \frac{\varepsilon_\nu}{\kappa_\nu} \\
&= -I_\nu + S_\nu
\end{aligned}
\tag{1.14}$$

For the case of a plane parallel atmosphere this is the equation of radiative transfer. Here $S_\nu = \frac{\varepsilon_\nu}{\kappa_\nu}$ and is called the source function. Clearly if $S_\nu > I_\nu$ the beam increases in energy. In thermodynamic equilibrium the Planck (black body) function is often chosen to represent S_ν .

In an AGB star the heat transport from the interior of the star into the atmosphere is achieved primarily by convection. However, the only way to transport energy from the surface of the star into the near vacuum of space, is by radiation. If we neglect emission by setting the source function to zero in equation 1.14 and integrate we obtain:

$$I_\nu(\tau_\nu) = I_\nu(0) \exp(-\tau_\nu) \tag{1.15}$$

Were $I_\nu(0)$ is the initial intensity of the radiation. This tells us that the radiation that we see does not originate much beyond an optical depth of $\tau_\nu = 2$ or 3. An optical depth of 2 or 3 corresponds to different distances for stellar atmospheres with different opacities. For example in the Sun this layer is of the order of 300 km thick compared to a solar radius of 700 000 km [61]. Therefore the observed spectrum of a star is formed only in the outermost layers of the star, known as the photosphere. It must also be noted that the temperature of the star changes with optical depth and hence atmospheric height. For example the temperature of the atmosphere of the sun at optical depths of $\tau(510 \text{ nm})=0.1$ and 1.5 is 5100 and 6700 K respectively [61]. Such a variation of temperature with optical depth can also be seen in the model C-star atmospheres of Eriksson *et al* [53], see figure 1.3.

The absorption coefficient κ_ν is dependent upon the composition of the gas, be it molecules, neutral atoms, ions or electrons. When calculating κ_ν it is highly important that no major sources of opacity are left out. For example the early works that left out a representation of HCN opacity in C-stars caused huge uncertainty in model atmospheres with $T_{eff} < 2800 \text{ K}$ [53]. It is therefore important that both the composition of the atmosphere and the spectrum of the major constituents of the atmosphere are well known.

1.4 The Need for more Data.

In the previous section it was mentioned why the spectrum of the constituents of a stellar atmosphere need to be well known. However for HCN there is a wealth of experimental data (see section 3.4). So why do we need more data? This is the question I seek to answer in this section.

The existing HCN opacity data that is currently in use is either: The *ab initio* opacity data of Jørgensen *et al* [54], recently used by Loidl *et al* [55], or compiled from available experimental data such as the linelist used by Aoki *et al* [16]. Both sets of data cover the most intense HCN transitions primarily the C-H stretch and bend fundamentals and some of their hot bands. The effects of these two modes at 3 and 14 μm can be seen in figures 7.10 and 1.2. The linelist that is based on experimental data used by Aoki *et al* [16] is likely to be more accurate than the *ab initio* data of Jørgensen [54]. However the data of Jørgensen *et al* covers all transitions between energy levels with less than 10 000 cm^{-1} compared to just the (01^10) , (02^00) , (100) , (01^11) , (100) - (01^10) transitions and some of their hot bands, covered by Aoki *et al* [16].

If both the linelist of Aoki *et al* [16] and the opacity data of Jørgensen *et al* [54] cover the strongest transitions then why do we need more data?

Although the most intense transitions are experimentally well studied, there are many weaker transitions of which the frequencies and intensities are unknown. Energy from a star will preferentially 'leak' out at frequencies at which there is little or no absorption. If these weaker transitions fall into a 'gap' in the absorption they will have a significant effect on the total opacity and energy transport within the atmosphere. The number of weak lines considerably outnumber the strongest lines. Consequently the fact that these lines are weak and many in number means that they are not covered in the experimental data. Further to this, at stellar temperatures ($T_{eff} \sim 2800 \text{ K}$), many of the weaker transitions will be between states with energy greater than 10 000 cm^{-1} . The calculations of Jørgensen *et al* [54] were a first attempt at opacity data and are inaccurate by todays standards (for example see table 5.13). It is important that the frequency of the lines and bands are accurate. If a weak line is incorrectly calculated to lie close to a strong line, then a 'gap' in absorption may be left which will have a significant effect on the opacity. Finally HNC has been neglected by all workers to date. Barber *et al* [62] have calculated the HNC/HCN ratio in thermodynamic equilibrium to be 0.05 and 0.34 for 2000 and 4000 K respectively. Furthermore the transitions of HNC are considerably stronger than

comparable transitions of HCN, increasing the likelihood that HNC will have an effect on opacity.

All the lines necessary for the construction of an accurate opacity function for HCN/HNC are simply too many in number ($\sim 10^8$) and impractical to measure for a Ph.D. thesis. Consequently, as was the opacity data of Jørgensen *et al*, the HCN/HNC linelist will be calculated via *ab initio* techniques.

Chapter 2

Calculating The Spectra of Triatomic Molecules.

It has been known for over a hundred years that atoms and molecules emit and absorb electromagnetic radiation at characteristic frequencies. It is this spectroscopic fingerprint which has allowed the identification of atoms and molecules in the observable universe. In fact helium was first identified as an unknown element in the spectrum of the Sun in 1868 by Sir William Crookes. He named the element helium from the Greek Helios meaning Sun. However, it was not until 1895 that Sir William Ramsey, working at University College London, isolated and identified helium in the lab. In chapter 1 it was discussed that the rotational lines of gas phase HNC were also first observed remotely, this time by radio astronomy.

It has been an ongoing process to understand the physics behind the spectra of atoms and molecules and to reproduce from first principles these spectra. The fundamentals of theory behind molecular spectra, in the form of the time independent Schrödinger equation (equation 2.1), have been in place for over 70 years.

$$\hat{H}\Psi = E\Psi \tag{2.1}$$

However the exact solutions to this equation, for anything more complex than two interacting particle systems, do not exist. Never-the-less, approximate solutions to the Schrödinger equation can be determined by a series of approximations. When considering molecules the first approximation that is made is the Born-Oppenheimer approximation.

2.1 The Born-Oppenheimer Approximation.

An atom is classically thought of as a nucleus surrounded by one or more electrons. For anything more complex than a hydrogenic atom, an atom with one electron, exact solutions to the Schrödinger equation do not exist. A molecule adds a further complication to this. A molecule has more than one nucleus and one or more electrons. Consequently exact solutions do not exist for any molecule. Born and Oppenheimer in 1927 [63] proposed a method of simplifying the problem for molecules. In the Born-Oppenheimer approximation the wavefunction of the molecule as a whole is separated into electronic and nuclear parts:

$$\Psi = \psi_n \times \psi_e \quad (2.2)$$

where Ψ is the total wavefunction and ψ_n and ψ_e are the nuclear and electronic wavefunctions respectively. Furthermore the Hamiltonian can also be separated into nuclear and electronic parts:

$$\hat{H} = \hat{T}_n + \hat{H}_e \quad (2.3)$$

where $\hat{T}_n$ is the nuclear kinetic operator part and $\hat{H}_e$ is the electronic part.

The Born-Oppenheimer approximation uses the fact that the mass of the electrons are small compared to the masses of the nuclei. Consequently the electrons can be thought of as moving considerably faster than the nuclei. This allows the supposition that the wavefunctions of the electrons instantly relax after a change in the nuclear geometry of the molecule.

If equations 2.2 and 2.3 are combined and manipulated (for example see Jensen [66]) one obtains:

$$(\hat{T}_n + E_e + U)\psi_n = E_t\psi_n \quad (2.4)$$

where E_t is the full eigen energy of the molecule, E_e is the solutions to the electronic Hamiltonian at a given nuclear geometry ($E_e = \langle \psi_e | \hat{H}_e | \psi_e \rangle$). The U term contains differentials of the electronic wavefunctions with respect to the co-ordinates of the nuclei. Within the Born-Oppenheimer approximation the term U is set to zero. In reality the ratio of U to E_e is of roughly the same order as the ratio of the mass of the electrons to the nuclei.

In this thesis a partial correction to the BO approximation has been fitted, see chapter 4. This correction considers only the diagonal parts of U and is called the Born-Oppenheimer diagonal correction (BODC). The non-diagonal parts of U couple different

electronic states and are less easy to calculate. The BODC is given by:

$$U = -\frac{1}{2} \sum_l \frac{\hbar^2}{m_l} \langle \psi_e | \nabla_l^2 | \psi_e \rangle \quad (2.5)$$

where the sum is over the nuclei, l , ψ_e is the electronic wavefunction and m_l is the mass of nuclei l .

The electronic potential energy can be determined at any given nuclear geometry. If many nuclear geometries are studied, an effective electronic potential energy surface (E_e in eq. 2.4) can be calculated and fitted. A fit for a HCN/HNC potential surface has been performed as part of this work and is reported in chapter 4.

The nuclear wavefunctions and rovibrational energy levels can now be determined from the electronic potential surface. The methods employed to determine the nuclear wavefunctions have evolved and been refined with time, but remain fairly complex. I will start with a discussion of perturbation theory.

2.2 Perturbation Theory.

In perturbation theory the full Hamiltonian is assumed to be approximately equal to, within a small perturbation, a Hamiltonian which has known solutions. For example see [64, 65]. Such that:

$$\hat{H} = \hat{H}_0 + \beta \hat{H}' \quad (2.6)$$

where β is a constant between 0 and 1, $\hat{H}$ is the full Hamiltonian, $\hat{H}_0$ is the Hamiltonian with known solutions and $\hat{H}'$ is the perturbing Hamiltonian. The accuracy of the method is dependent upon the choice of $\hat{H}_0$. If $\hat{H}_0$ is very close to $\hat{H}$ then the perturbation $\hat{H}'$ is small compared to $\hat{H}_0$ and the approximation will be good.

It is usual that the eigen energy and wavefunction is expanded in a power series, so that:

$$\psi = \psi_0 + \beta \psi_1 + \beta^2 \psi_2 + \dots \quad (2.7)$$

and

$$E = E_0 + \beta E_1 + \beta^2 E_2 + \dots \quad (2.8)$$

where E_0 and ψ_0 are the zero order eigen energy and wavefunction, which are the solutions to $\hat{H}_0$. Perturbation theory is only useful if the series converge, so that it can be truncated after some small number of terms.

When perturbation theory is applied to vibration-rotation motion, the vibrational and rotational parts are often separated. Often harmonic oscillation functions are used for the unperturbed vibrational potential and rigid rotors are often used for the unperturbed rotational Hamiltonian. The harmonic oscillator and rigid rotor will be briefly discussed here.

The vibrational potential is first expanded about the equilibrium distance, r_e , so that for the 1D case, the potential is:

$$V = V(r_e) + K_1(r - r_e) + \frac{1}{2}K_2(r - r_e)^2 + \frac{1}{6}K_3(r - r_e)^3 + \dots \quad (2.9)$$

here the K_n correspond to the derivatives of the potential $K_n = \frac{d^n V(r_e)}{dr_e^n}$. These derivatives are often called the force constants. $V(r_e)$ can be defined to be zero and the first derivative (K_1) evaluated at the minimum is zero. This leaves only the second and higher order terms. Clearly the second order term is the harmonic oscillator potential so higher terms can be considered a perturbation on the harmonic potential. If a potential contains third order and higher terms it is called an anharmonic potential.

The harmonic potential is defined by:

$$V = \frac{1}{2}K_2(r - r_e)^2 \quad (2.10)$$

where K_2 is a constant, r is the distance separating the nuclei and r_e is the distance between the nuclei at the minimum of the potential. The energy levels for this potential for the 1D and the degenerate 2D cases are well known [65, 67]. They are, for 1D:

$$E_v = h\omega(v + \frac{1}{2}) \quad (2.11)$$

and for the degenerate 2D case:

$$E_v = h\omega(v + 1) \quad (2.12)$$

where $v = 0, 1, 2, 3, \dots$ is the vibrational quantum number, ω is the harmonic frequency where $\omega^2 = \frac{K}{4\pi^2\mu}$, μ is reduced mass and h is Planck's constant. When $v = 0$, the 1D harmonic oscillator has energy $E_0 = \frac{1}{2}h\omega$ which is non-zero. This is an important result, the harmonic oscillator never has zero energy, it always has some vibrational motion. This minimum energy is called the zero point energy.

The choice of the harmonic potential as a first approximation is relatively good at low energies. However, for high energies the harmonic potential is a poor representation of the true potential and deviates hugely from the true potential. Therefore at high energies, the

requirement of perturbation theory that $\hat{H}_0 \gg \hat{H}'$ breaks down. Although perturbation theory may be useful in some regions of a potential it is not usually globally valid.

For the rotational motion it is common that the rigid rotor be used for the unperturbed Hamiltonian. The solutions to the rigid rotor problem are well known, a complete discussion is given in Gordy and Cook [127]. The Hamiltonian of the fully linear rigid rotor is:

$$\hat{H}_0 = \frac{\hat{L}^2}{2I} \quad (2.13)$$

where $\hat{L}^2$ is the square of the total angular momentum operator and I is the moment of inertia of the molecule. The eigen energies are $BJ(J+1)$, where B is the rotational constant and J is the total angular momentum quantum number. However a real molecule is not-rigid, there is a degree of distortion, induced by both vibration and rotation. One of the first problems that arises with the linear rigid rotor is vibrational induced non-linearity, discussed in chapter 3. If we consider that the molecule has become slightly bent then a moment of inertia (I_z) along the body fixed z axis exists and must be accounted for. The perturbing Hamiltonian is:

$$\hat{H}_z = -\frac{1}{2I} \hat{L}_z^2 \quad (2.14)$$

where $\hat{L}_z^2$ is the square of the z projection of the angular momentum operator. The eigen values of $\hat{H}_z$ are $-Bl^2$ where l is the vibrational angular momentum. The expression for this slightly nonlinear rigid rotor is given in eq. 3.1. Further to the vibrationally induced non-linearity is the centrifugal distortion. As the molecule rotates a centrifugal force acts to stretch the bond lengths. Further perturbing Hamiltonian's are needed to account for this. These perturbing Hamiltonian's are proportional to $(\hat{L}^2 - \hat{L}_z^2)^n$. The first of these is $n = 2$ and is the centrifugal distortion. The expression for the rotational energy levels of this slightly nonlinear centrifugally distorted rotor is given in equation 3.3. This describes the rotational motion of a molecule in a given vibrational state very well at low energies. However at high rotational excitations we have the situation where the higher terms of equation 3.3 are of the order of the first term or greater. At this point the requirement of perturbation theory that $\hat{H}_0 \gg \hat{H}'$ breaks down. Furthermore there is no account of the vibration-rotation coupling. For example vibrationally averaged equilibrium geometry changes from vibrational state to state, so that the moment of inertia of the molecule is different in different vibrational states. This problem manifests itself in the fact that B_v , D_v and higher terms change with vibrational state. There

is also the problem of l -type resonance and doubling (see section 3.1). The rotation-vibration coupling is often accounted for by again considering small displacements from equilibrium. This allows the determination of what are called Coriolis coupling terms. However for high vibrational excitation, displacement from equilibrium may be large. For example the highly excited bending modes of HCN and in fact the so called delocalised states have very large displacements from equilibrium. Perturbation theory will not be able to account for these large deviations from the minimum.

Much work has been done on approximations to the full Hamiltonian that are more sophisticated than the harmonic oscillator and the rigid rotor. However even these more sophisticated applications of perturbation theory suffer from the same problems as their less sophisticated counterparts as a result of a large amplitude motion, for example see [69, 70].

In general perturbation theory remains a useful tool. At low energies perturbation theory describes the rotational and vibrational motion reasonably well, for example [71]. It gives rise to the assignment of the approximate quantum numbers that are given in section 3.1. Experimentalists still fit their data with rotational and force constants as a way of reducing the amount of data that needs to be presented. However highly rotationally and vibrationally excited states, which have large amplitude motion, are likely to be poorly described by perturbation theory, see refs [69, 70]. Therefore perturbation theory will not be used for this work.

2.3 Variational Techniques.

Perturbation theory makes the approximation that the solutions to the full Hamiltonian are, within some small perturbation approximately equal to the known solutions of a similar Hamiltonian. In contrast variational techniques aim to obtain “exact” solutions to the full Hamiltonian. Variational techniques first guess an eigen function as a solution to the Hamiltonian, then improve that guess. This is achieved via the variational principle, first introduced by Lord Rayleigh [68]. If we consider a normalised wavefunction ϕ as an approximation to the exact wavefunction of the ground state, ψ_0 . The expectation value of ϕ is:

$$\epsilon = \int \phi^* \hat{H} \phi d\tau \quad (2.15)$$

where $\hat{H}$ is the full Hamiltonian. As the exact wavefunctions (ψ_n) of $\hat{H}$ are a complete orthonormal set, so ϕ can be expanded as:

$$\phi = \sum_n a_n \psi_n \quad (2.16)$$

where a_n are the parameters that are to be determined. Substituting equation 2.15 into equation 2.16 we obtain:

$$\begin{aligned} \epsilon &= \int \sum_n a_n^* \psi_n^* \hat{H} \sum_m a_m \psi_m d\tau \\ &= \sum_{nm} a_n^* a_m \int \psi_n^* \hat{H} \psi_m d\tau \end{aligned} \quad (2.17)$$

$$(2.18)$$

Via the fact that $\hat{H}\psi_n = E_n\psi_n$, where E_n is the eigen energy of the n^{th} state, and orthonormality $\int \psi_n^* \psi_m d\tau = \delta_{nm}$ we obtain:

$$\begin{aligned} \epsilon &= \sum_{nm} a_n^* a_m E_n \delta_{nm} \\ &= \sum_n |a_n|^2 E_n \end{aligned} \quad (2.19)$$

By the fact that ϕ has been chosen to be orthonormal $\int \phi^* \phi d\tau = \sum_n |a_n|^2 = 1$. E_0 is next subtracted from both sides of equation 2.19, so that:

$$\begin{aligned} \epsilon - E_0 &= -E_0 + \sum_n |a_n|^2 E_n \\ &= \sum_n -|a_n|^2 E_0 + \sum_n |a_n|^2 E_n \\ &= \sum_n |a_n|^2 (E_n - E_0) \end{aligned} \quad (2.20)$$

As $|a_n|^2 \geq 0$ we obtain the important result of the variational principle:

$$\epsilon \geq E_0 \quad (2.21)$$

The energy of the approximate solution for the ground state is greater than or equal to the energy of the true ground state. Therefore, by minimising ϵ , we can obtain the best possible approximation to the true ground state energy. For a more detailed discussion of the above derivation see Schiff [65] and Rae [64]. The variational principle can be extended to the n^{th} state so that equation 2.21 becomes $\epsilon_n \geq E_n$, for example see Macdonald [72], allowing the determination of good solutions for the excited state.

The choice of the starting wavefunctions is very important within variational techniques. It is usual to expand each of the wavefunctions into a sum of what are called basis functions. Each basis function has parameters which can be changed to minimise the energy eigen value. Clearly to be numerically solvable there can only be a finite number of basis functions. This is called the finite basis representation (FBR).

2.4 Finite Basis Representation.

In FBR the wavefunctions usually expanded as a series of basis functions which are linear in the parameters c_i .

$$\begin{aligned}\psi &= c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \dots + c_n\phi_n \\ &= \sum_i^n c_i\phi_i\end{aligned}\tag{2.22}$$

Where values for the parameters c_i need to be determined so that the expectation energy is minimised. For a full discussion of the following derivation see ref [73]. The expectation energy of ψ is given by:

$$\begin{aligned}\epsilon &= \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \\ &= \left[\sum_{ij} c_i^* c_j \int \phi_i^* \phi_j d\tau \right]^{-1} \sum_{ij} c_i^* c_j \int \phi_i^* \hat{H} \phi_j d\tau\end{aligned}\tag{2.23}$$

Where $\int \phi_i^* \hat{H} \phi_j d\tau = H_{ij}$ are the matrix elements of the Hamiltonian matrix $\mathbf{H}$. The constants c_i and wavefunctions ϕ_i are assumed to be real so that $c_i^* = c_i$, and $\int \phi_i^* \phi_j d\tau = \int \phi_i \phi_j d\tau = S_{ij}$ where S_{ij} is called the overlap integral. Minimising the expectation energy is simply a matter of finding the solutions of:

$$\frac{\partial \epsilon}{\partial c_k} = 0\tag{2.24}$$

By multiplying equation 2.23 by $\sum_{ij} c_i^* c_j \int \phi_i^* \phi_j d\tau$ and differentiation with respect to c_k we have:

$$\epsilon \frac{\partial}{\partial c_k} \sum_{ij} c_i c_j S_{ij} = \frac{\partial}{\partial c_k} \sum_{ij} c_i c_j H_{ij}\tag{2.25}$$

If the basis functions are chosen to be orthonormal then the overlap integral $S_{ij} = \delta_{ij}$. Including this and differentiating equation 2.25 yields a set of n simultaneous equations with n unknowns. These simultaneous equations can be encapsulated in matrix notation by:

$$\mathbf{H}\mathbf{c} = \epsilon\mathbf{c} \quad (2.26)$$

where $\mathbf{c}$ is an n dimensional vector the elements of which are the coefficients c_k . Here ϵ is an eigen value of $\mathbf{H}$ and $\mathbf{c}$ is the eigen vector. The elements of the Hamiltonian matrix $\mathbf{H}$ are $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$ and the integral is evaluated via numerical integration. The basis functions ϕ_i are usually chosen so that Gaussian quadrature may be used to evaluate the matrix elements [152].

The Hamiltonian matrix $\mathbf{H}$ may have more than one eigen value and eigen vector. The equation can be extended to encompass m eigen values and eigen vectors:

$$\mathbf{H}\mathbf{C} = \mathbf{C}\epsilon \quad (2.27)$$

where $\mathbf{C}$ is now a matrix of m $\mathbf{c}$ vectors and ϵ is an m by m diagonal matrix, the diagonal elements of which are the eigen values of $\mathbf{H}$. Multiplying both sides by $\mathbf{C}^{-1}$ yields:

$$\mathbf{C}^{-1}\mathbf{H}\mathbf{C} = \epsilon \quad (2.28)$$

so that the mathematical operation of obtaining ϵ and $\mathbf{C}$ is called the diagonalisation of the Hamilton matrix.

The relative position of the nuclei in triatomic molecules can be described by three internal co-ordinates. Consequently for triatomics the vibrational basis functions are usually described as the product of three functions of each co-ordinate. So that the wavefunction, ψ , is:

$$\psi(q_1, q_2, q_3) = \sum_i \sum_j \sum_k c_{ijk} \phi'_i(q_1) \phi'_j(q_2) \phi'_k(q_3) \quad (2.29)$$

where the q_1 , q_2 and q_3 are the internal co-ordinates of the system. The elements of the Hamiltonian matrix are then $\langle \phi_i \phi_j \phi_k | \hat{H} | \phi'_i \phi'_j \phi'_k \rangle$.

An example of such a calculation performed on HCN is that of Carter *et al* [136]. Carter *et al* used vibrational basis functions that were the product of Morse oscillators for the radial co-ordinates and Legendre polynomials for the angular co-ordinate. If vibration-rotation levels are to be calculated it is also important to include a rotational factor in the basis functions. Carter *et al* [136] for HCN used symmetric top rotational functions.

The level of accuracy of FBR is dependent upon the number of basis functions used. The wavefunction ψ will more closely resemble the true wavefunction if more basis functions are used. Consequently the calculated eigen energy converges towards the true eigen energy as the number of basis functions are increased.

High lying states, have large amplitude motion (LAM) [85], so require more basis functions to converge than low energy levels. The size of Hamiltonian matrix is a function of m^2 , where m is the number of basis functions. Thus the size of the Hamiltonian required for the convergence of the LAM states quickly increases, as does the required computer resources. So that the level to which FBR calculations can be taken is heavily limited by the available computer resources.

2.5 Discrete Variable Representation.

To overcome the Hamiltonian matrix size problems of FBR, Light *et al* [74] implemented discrete variable representation (DVR) in the field of molecular spectroscopy. In FBR the wavefunctions are represented by the coefficients of the basis functions. Dickinson and Certain [78] proved that for a basis set of $(J_{max}+1)$ classical orthogonal polynomials there exists a transformation to $(J_{max} + 1)$ orthogonal weighted Gaussian quadrature points for the relevant function. DVR uses this theorem to express the wavefunctions in terms of a basis consisting of discrete points. In DVR the calculation can be performed as a series of diagonalisations and truncations of 1D, 2D and then 3D Hamiltonian matrices, see Bačić and Light [76]. Thereby reducing the size of the 2D and 3D Hamiltonians and so reducing the overall size of the calculation. For example, for a 3D Hamiltonian one co-ordinate can be frozen and the Hamiltonian solved first in 2D. The 2D wavefunctions can then be truncated by removing the points at which the wavefunction has no magnitude. Thereby reducing the size of the full 3D Hamiltonian. This results in a matrix size reduction and consequently an improvement in efficiency over FBR techniques [75]. Furthermore as a result of what is called the quadrature approximation the potential matrix elements in DVR are diagonal [75], so easily evaluated.

To obtain the Hamiltonian matrix in a DVR, the FBR Hamiltonian matrix is transformed into the DVR, by the methods proposed by Harris *et al* [77]. If we define the 3D DVR grid points as (α, β, γ) , then the matrix elements of the 3D DVR Hamiltonian are:

$$H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'}^{DVR} = \sum_{m,n,j} \sum_{m',n',j'} T_{n,m,j}^{\alpha,\beta,\gamma} H_{m,m',n,n',j,j'}^{FBR} T_{m',n',j'}^{\alpha',\beta',\gamma'} \quad (2.30)$$

where $T_{m,n,j}^{\alpha,\beta,\gamma}$ are the elements of the transformation matrix. The 3D transformation matrix can be factorised into its 1D parts:

$$T_{m,n,j}^{\alpha,\beta,\gamma} = T_m^\alpha T_n^\beta T_j^\gamma \quad (2.31)$$

the 1D transformation matrices are related to the Gauss quadrature points and weights of the respective function by:

$$T_t^\zeta = \sqrt{\omega_\zeta} |t(\zeta)\rangle \quad (2.32)$$

where $|t\rangle = |m\rangle, |n\rangle, |j\rangle$ and $\zeta = \alpha, \beta, \gamma$ and ω_ζ is the weight of the Gaussian quadrature. Hence one can freely transform between an FBR and a DVR. The wavefunction and Hamiltonian of each co-ordinate can be expressed in either DVR or FBR basis sets, so that for example two dimensions can be represented by DVR and the third in FBR [75]. This allows one to choose the most useful representation or combination of representations for the task in hand.

2.6 Calculation of Line Strength of Electric Dipole Transitions.

The line strength [122] between rotationally degenerate states ψ and ψ' is given by:

$$S(f-i) = (2J+1)(2J'+1) \langle \psi | \underline{\mu} | \psi' \rangle^2 \quad (2.33)$$

where $S(f-i)$ is the line strength and $\underline{\mu}$ is the electric dipole moment vector. The line strength is related to absolute intensity by the expressions in section 3.3. If the wavefunctions have been determined the calculation of the transition dipole is simply a matter of performing the integration in equation 2.33.

In a 3D FBR where the basis functions are $|\psi_m\rangle$, $|\psi_n\rangle$ and $|\psi_j\rangle$ and the i^{th} wavefunction is $\psi^i = \sum_{nmj} \psi_n^i \psi_m^i \psi_j^i = \sum_{nmj} \psi_{nmj}^i$. Then equation 2.33 becomes:

$$S(f-i) = (2J+1)(2J'+1) \left(\sum_{n,m,j} \sum_{n',m',j'} \langle \psi_{n,m,j} | \underline{\mu}(r_1, r_2, \theta) | \psi_{n',m',j'}' \rangle \right)^2 \quad (2.34)$$

This is a 6 dimensional summation which requires the integral $\langle \psi_{n,m,j} | \underline{\mu}(r_1, r_2, \theta) | \psi_{n',m',j'}' \rangle$ to be evaluated $N_n^2 \times N_m^2 \times N_j^2$ times for each transition. Where N_n , N_m and N_j are the number of n , m and j basis functions respectively. For the calculation of a linelist involving hundreds of millions of transitions this would simply be too time consuming to solve. However Schwenke [81] suggested reducing the dimensionality of the problem to

reduce the run time. If the FBR is transformed to fully DVR, the problem is massively simplified. For example Lynas-Gray *et al* [80] performed intensity calculations on water using a DVR basis for the radial co-ordinates and an FBR basis for the angular co-ordinate. Lynas-Gray *et al* found that this gave a factor of 80 time saving over the FBR calculation. This can be extended so that the whole calculation can be performed in DVR [123]. However the contribution of the angular j components of the FBR and hence γ components of the DVR, have a k dependence, see equation 2.36. This makes a further transformation into an angular integration grid which is independent of k , necessary. The time savings of a full DVR are a result of the application of the quadrature approximation in which the matrix elements $\langle \psi_{\alpha,\beta,\gamma_0} | \underline{\mu}(r_{1\alpha}, r_{2\beta}, \theta_{\gamma_0}) | \psi'_{\alpha',\beta',\gamma_0'} \rangle$ are diagonal:

$$\begin{aligned}
S(f-i) &= (2J+1)(2J'+1) \left(\sum_{\alpha,\beta,\gamma_0} \sum_{\alpha',\beta',\gamma_0'} \langle \psi_{\alpha,\beta,\gamma_0} | \underline{\mu}(r_{1\alpha}, r_{2\beta}, \theta_{\gamma_0}) | \psi'_{\alpha',\beta',\gamma_0'} \rangle \delta_{\alpha,\alpha'} \delta_{\beta,\beta'} \delta_{\gamma_0,\gamma_0'} \right)^2 \\
&= (2J+1)(2J'+1) \\
&\quad \times \left(\sum_{\alpha,\beta,\gamma_0} [\psi_{\alpha,\beta,\gamma_0} \psi'_{\alpha,\beta,\gamma_0} \mu_x(r_{1\alpha}, r_{2\beta}, \theta_{\gamma_0}) + \psi_{\alpha,\beta,\gamma_0} \psi'_{\alpha,\beta,\gamma_0} \mu_z(r_{1\alpha}, r_{2\beta}, \theta_{\gamma_0})] \right)^2 \quad (2.35)
\end{aligned}$$

where μ_x and μ_z are the x and z components of the dipole moment vector, this new angular grid is denoted here as γ_0 . This reduction in dimensionality will clearly result in massive time saving. A further saving over FBR is obtained, because the wavefunctions and dipole moment need only be evaluated and multiplied at the grid points. The dipole calculations performed in this work are the most time consuming part. Without the advantages of DVR over FBR the calculation of the linelist in this work would not have been possible.

2.7 The DVR3D suite.

The DVR3D suite was developed by Tennyson and co-workers [122, 123] for nuclear motion calculations on triatomic molecules. The codes are an application of DVR to the rotational vibrational motion of triatomic molecules. The determination of the coupled rotation-vibration motion is performed in two steps. The first step is the determination of the Coriolis decoupled (vibrational) wavefunctions, performed by the DVR3DRJZ module. ROTLEV3 performs the second step, in which the wavefunctions are Coriolis coupled, yielding the full rotation-vibration wavefunctions. There are further modules which perform other functions such as the calculation of transition dipoles and spectra. The calculations can be performed in standard or symmeterised Radau or Jacobi co-ordinates. Four of the modules of the DVR3D suite are used in this thesis and discussed here.

2.7.1 DVR3DRJZ.

DVR3DRJZ performs the first step in the fully pointwise calculation of the rotation-vibration wavefunctions. The first part of which is the construction of the Hamiltonian matrix.

The Hamiltonian matrix of a triatomic molecule in FBR can be expressed as [122]:

$$\begin{aligned} \langle n, m, j, k, J | \hat{H} | n', m', j', k', J \rangle &= \delta_{k,k'} \langle m, n, j | \hat{H}^{J,k} | m, n, j \rangle \\ &+ \delta_{j,j'} \delta_{s,s'} \delta_{k',k \pm 1} (1 + \delta_{k,0} + \delta_{k',0})^{-1/2} C_{J,k'}^{\pm} C_{j,k'}^{\pm} \\ &\times \langle t | g^{(i)} | t' \rangle \end{aligned} \quad (2.36)$$

where n and m are the radial basis functions, j is the angular basis function, k is the quantum number of the projection of the total angular momentum onto the z axis and J is the total angular momentum. Parity has been neglected for clarity. The functions $C_{l,k}^{\pm}$ are given by:

$$C_{l,k}^{\pm} = (l(l+1) - k(k \pm 1))^{1/2} \quad (2.37)$$

The operator $\hat{g}^{(i)}$ is:

$$\hat{g}^{(i)} = \frac{\hbar^2}{2\mu_i r_i^2} \quad (2.38)$$

where $|t\rangle$, s and i depend along which radial co-ordinate the z axis is embedded, for the z axis embedded along r_1 , $|t\rangle = |m\rangle$, $s = n$ and $i = 1$. Conversely for the embedding along r_2 , $|t\rangle = |n\rangle$, $s = m$ and $i = 2$. μ_i is the reduced mass.

DVR3DRJZ diagonalises the first, diagonal in k , term of equation 2.36 in the full DVR for a given value of J and at each possible value k . This is the implementation of a two step procedure, that was first proposed by Tennyson and Sutcliffe [79], in which k is assumed to be a good quantum number. The first term of equation 2.36 is called the Coriolis decoupled Hamiltonian and is converted to DVR by the transformation $\mathbf{T}^T \mathbf{H} \mathbf{T}$, see section 2.5. For $J = 0$ the second term of equation 2.36 is zero, so that the full solutions are simply the solutions of the Coriolis decoupled Hamiltonian. The elements for this transformed Hamiltonian matrix are given in [122].

With the DVR Hamiltonian matrix obtained the next step in its solution is the diagonalisation of the 1D Hamiltonians. Which allows the truncation of the 2D Hamiltonian at the points at which the 1D wavefunctions have no magnitude. The 2D Hamiltonians are then diagonalised and the 3D Hamiltonian truncated. The 3D Hamiltonian is then diagonalised and the wavefunctions and eigenvalues stored for the second step. DVR3D allows the user to choose the order in which the co-ordinates are solved. For example, in

this work for HCN the Hamiltonian is solved in the order r_1, r_2, θ . So that α is diagonalised for each β, γ .

2.7.2 ROTLEV3.

ROTELEV3 performs the second step in the solution of equation 2.36, to obtain the full rotation-vibration wavefunctions and energy-eigenvalues. The first term of equation 2.36 are obtained by DVR3DRJZ, simplifying the construction of the full Hamiltonian. The second term of equation 2.36 is diagonal in the angular FBR but not in the angular DVR. Conversely the factor $\langle t | \hat{g}^{(i)} | t' \rangle$ in the second term of equation 2.36, is, as a result of the quadrature approximation, diagonal in the radial DVR [85]. So to save on computational load the DVR wavefunctions generated by DVR3DRJZ need to be transformed into FBR in the angular co-ordinate whilst remaining in DVR in the radial co-ordinates. The full Hamiltonian matrix is sparse that is most of the off-diagonal terms are zero. Consequently only the diagonal elements and the $(k \pm 1)$ are computed and stored. In ROTLEV3 the diagonalisation is usually performed via an iterative routine which has proved successful [122].

The eigen vector solutions of the second step are then transformed back into the original DVR basis used by DVR3DRJZ and saved with the energy eigenvalues for later use. The subroutine which performs this final part of ROTLEV3 was modified during this work, see section 5.3.1, so that a more recent and faster version of DIPOLE3 could be used.

2.7.3 DIPOLE3.

Using the wavefunctions from ROTLEV3, DIPOLE3 performs a summation of the type in equation 2.35 for each $k - k'$ -overlap and each energy level, to obtain $S(f - i)$, from which line intensities can be calculated.

The first step in DIPOLE3 is to convert the DVR wavefunctions from ROTLEV3 onto a new integration grid. In this integration grid the radial points are the radial DVR points but the angular points are changed to a new basis. The amplitude of the wavefunction and the dipole moment at each integration point is calculated and the summation is performed. The results of the summation are saved along with the energies of the levels involved in the transition, for use by SPECTRA.

The most time consuming part of DIPOLE3 is the multiplication and summation of wavefunction amplitudes and dipole moments, for example see equation 2.35. This is

performed in part of the subroutine TRANS. During the course of this work the time consuming part of TRANS was parallelised, to reduce the overall run time of DIPOLE3, see section 5.3.3.

2.7.4 SPECTRA.

Spectra converts the $S(f - i)$ output from DIPOLE3 into frequency ordered relative intensities and intensities in cm molecule^{-1} . There is the option to generate line profiled or stick absorption or emission spectra. Finally there is also an option to calculate a partition function from input of energy levels from ROTLEV3.

During the course of this work SPECTRA was converted from FORTRAN77 to FORTRAN90 and the frequency sorting routines were changed, see section 5.3.4.

2.8 The Co-ordinate System.

The potential energy surface of the HCN molecule has two minima and a saddle point, see fig 4.6. The global energy minimum is linear HCN and linear HNC is located at the secondary minimum. The H nucleus in excited vibrational states tends to undergo large amplitude motion. In particular, the bending mode of the nucleus at high excitation moves through large angular displacements. In higher yet excitations the H nucleus becomes delocalised about the CN diatom. Furthermore we wish to study HNC at the same time as HCN.

The choice of co-ordinates should be made so as to simplify as much as possible the description of the vibrational modes in the co-ordinate system. So ideally each vibration should be described by motion in one of the co-ordinates. Such a co-ordinate system is difficult if not impossible to define. Consequently we seek to describe each vibrational mode as closely as possible by just one of the co-ordinates of the co-ordinate system. Of the available co-ordinates systems Jacobi or scattering co-ordinates seem to be the best choice.

The Jacobi co-ordinate system is illustrated in figure 2.1. Three co-ordinates describe the position of the nuclei. These are r which we chose as the C to N distance, R which is the H to CN center of mass distance and finally γ the angle between R and r . In this work γ is defined so that $\gamma = 0$ is HCN and $\gamma = \pi$ is HNC.

In Jacobi co-ordinates the CN stretch mode can be predominantly described as a vibration in the r co-ordinate. Likewise the H-C or H-N vibration can be described as a

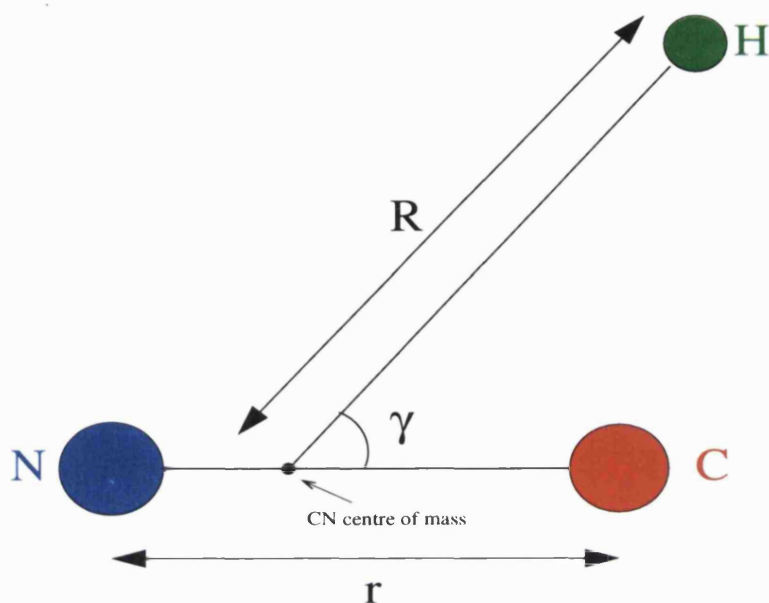


Figure 2.1: Jacobi or scattering co-ordinates for HCN.

vibration in the R co-ordinate. Finally the bending mode is predominantly described by the angular co-ordinate.

2.9 Potential and Dipole Surfaces.

The potential energy surface (PES) is vital to the construction of the rotation-vibration Hamiltonian. Electronic energies at various nuclear geometries are generated in the first step of the Born-Oppenheimer approximation, see section 2.1. These potential energy points are then fitted to obtain a continuous potential energy function, see chapter 4.

The dipole moment surface (DMS) is generated in a similar fashion to the PES. The dipole moment of the molecule is calculated at a set of nuclear geometries. These points are then fitted to obtain a continuous dipole function.

The accuracy of both the potential and dipole surfaces is vitally important. The surfaces set the maximum level of accuracy which can be obtained from the nuclear motion calculations. If for example the potential surface is poor then the rotational-vibrational energy levels and wavefunctions will be poor. It is therefore important that the electronic calculations are good and that the surface is well fitted. Electronic structure calculations

were not performed in this work. However the results of electronic structure calculations, were used to fit a new PES, DMS, relativistic and adiabatic correction surfaces, see chapter 4.

2.10 Fitting A Surface.

The most common methods used to generate a potential surface from a set of points are: the cubic spline interpolation and least squares fitting.

2.10.1 Linear Least Squares Fitting.

In least squares fitting a function is chosen that is believed to be similar in shape to the data that is being fitted. The fitting function is adjusted so as to minimise the sum of the squares of the deviation of the function from the data point. For example:

$$S^2 = \sum_i^N (y_i - f(x_i))^2 \quad (2.39)$$

where S^2 is the sum of the squares, x_i and y_i are the points to be fitted and $f(x)$ is the fitting function where $f(x_i) \sim y_i$.

The quality of a least squares fit is dominated by the choice of fitting function. A good choice of fitting function will maximise the quality of the fit whilst minimising both the number of fitting parameters needed and the number of points required for the fit. However the reverse is true if the function that is chosen is a poor representation of the fitted data.

For a 1D fit to a set of points defined by (x_i, y_i) linear least squares fitting uses a fitting function:

$$y_i \approx f(x_i) = \sum_j^m a_j X_j(x_i) \quad (2.40)$$

where $X_j(x_i)$ are any functions of x_i , and a_j are a set of parameters. In linear least squares the fitting function must be linear in a_j , but the functions X_i can be highly non-linear. Substituting equation 2.40 into 2.39 gives:

$$S^2 = \sum_i^n [y_i - \sum_j^m a_j X_j(x_i)]^2 \quad (2.41)$$

To minimise S^2 we must differentiate with respect to all a_j and equate to zero. Which gives us m simultaneous equations of the form:

$$\sum_i^n X_k(i) \left[y_i - \sum_j^m a_j X_j(x_i) \right] = 0 \quad (2.42)$$

Rearranging gives:

$$\sum_i^n X_k(i)y_i = \sum_i^n X_k(i) \sum_j^m a_j X_j(x_i) \quad (2.43)$$

These simultaneous equations can be written as a matrix-vector multiplication:

$$\mathbf{A}\mathbf{a} = \mathbf{b} \quad (2.44)$$

where the elements of $\mathbf{a}$ are simply the coefficients a_j and the elements of the matrix $\mathbf{A}$ and vector $\mathbf{b}$ are:

$$A_{jk} = \sum_i^n X_j(x_i)X_k(x_i) \quad (2.45)$$

$$b_k = \sum_i^n y_i X_k(x_i) \quad (2.46)$$

So finding the coefficients of the least squares fit is simply a matter of constructing $\mathbf{A}$ and $\mathbf{b}$, then inverting $\mathbf{A}$ and multiplying by $\mathbf{b}$. There are many algorithms for calculating the inverse of a matrix, for example see Press *et al* [82]. In the fitting program used in this work LU-decomposition followed by back substitution was used, again see Press *et al* [82].

Some data may be desired to be fitted more closely than most of the other data, or vice-versa. In such cases a 'weighting' factor can be assigned to the data. The weight represents the priority that the data has in the fit. Data with a higher weight is fitted more closely than data with a lower weight. This can be achieved simply by multiplying the square of the deviation of the fitting function from the data: $(y_i - f(x_i))^2$ by the weighting factor. The sum of the squares given by equation 2.41, becomes:

$$S^2 = \sum_i^n w_i [y_i - \sum_j^m a_j X_j(x_i)]^2 \quad (2.47)$$

where w_i is the weighting factor of the data point. The elements of the $\mathbf{A}$ matrix and the $\mathbf{b}$ vector, given by equations 2.45 and 2.46 become:

$$A_{jk} = \sum_i^n w_i X_j(x_i)X_k(x_i) \quad (2.48)$$

$$b_k = \sum_i^n w_i y_i X_k(x_i) \quad (2.49)$$

This method of weighting increases the data points contribution to the sum of squares by w_i . If w_i is an integer, this is identical to including the data point w_i times in the data to be fitted. So as a result forces the data point to be fit more closely than data with a lower weighting.

It is a simple matter of extending linear least squares to several dimensions. For example for a 3D potential V_i at points x_i, y_i, z_i the function X simply becomes a function of 3 co-ordinates, i.e. $X(x_i, y_i, z_i)$. However many more points and terms in the fitting function are required to fit 3D surfaces than 1D surfaces.

For a more thorough discussion of least squares fitting and LU-decomposition the reader is referred to Press *et al* [82].

Linear least squares fitting was used to fit the relativistic and BODC surfaces and for most of the coefficients of the fit for the PES and DMS.

2.10.2 Non-Linear Fitting.

If a set of points is best fitted by a non-linear combination of the fitting coefficients. Then the relatively simple linear least squares method cannot be used. An example of such a fitting function is the Gaussian $a_1 \exp(-[a_2 + a_3 x_i]^2)$, which cannot be fitted with linear least squares. In this work an iterative method was used. This method makes a step down the gradient of S^2 for each parameter, in order to minimise S^2 , for example see ref [82]. So that:

$$\mathbf{a}_{next} = \mathbf{a}_{last} - C \nabla S^2(\mathbf{a}_{last}) \quad (2.50)$$

where $\mathbf{a}_{next}$ is the improved set of coefficients, $\mathbf{a}_{last}$ is the previous set of coefficients and C is a constant. The constant C must be chosen so that the step does not step over the minimum. This method was used to fit the dipole surface and as part of the fit for the PES see chapter 4.

2.10.3 Spline Interpolation Vs Least Squares Fitting.

The cubic spline uses an interpolation between points that is smooth in the first derivative and continuous in the second derivative. It has the advantage that it passes directly through the points and is relatively easy to perform on any well behaved set of points. However it requires a larger number of points to obtain the same quality of surface as one would obtain with a least squares fitting using a well chosen fitting function. This is because when using least squares fitting you are able to put in knowledge about the general shape of the surface to be fitted through the choice of fitting function. The spline assumes no knowledge of the shape of the data to be fitted. An added bonus of least squares fitting is that one obtains a standard deviation of the fit from the points. This provides an indication of the accuracy of the fit.

As high quality electronic calculations are computationally expensive, only relatively few points can be calculated. Therefore least squares fitting will be used to fit the surfaces, so as to obtain the best fit with few points.

2.11 Morphing a Surface.

Gazdy and Bowman [108] and Meuwly and Hutson [109], introduced a technique for improving potential energy surfaces with a few highly accurate points. In this technique the original potential energy surface is effectively used as a fitting function for a least squares fit to a few highly accurate points. Meuwly and Hutson [109] used the following expression to morph their Ne-HF PES:

$$V_{morph}(R, \theta) = \nu(R, \theta)V_{orig}(\rho(\theta)R, \theta) \quad (2.51)$$

where $\nu(R, \theta)$ is the energy scaling function and $\rho(\theta)$ is the length scaling parameter which are given by:

$$\nu(R, \theta) = \sum_{\lambda, k} \nu_{\lambda, k} P_{\lambda}(\cos \theta) f_k(R) \quad (2.52)$$

and

$$\rho(\theta) = \sum_{\lambda} \rho_{\lambda} P_{\lambda}(\cos \theta) \quad (2.53)$$

where $\nu_{\lambda, k}$ and ρ_{λ} are the fitting parameters, $P_{\lambda}(\cos \theta)$ are Legendre polynomials and $f_k(R)$ is some function of R . Meuwly and Hutson [109] found that by using this technique they were able to hugely improve their PES, with a few high accuracy points.

Morphing has been used to improve the PES in this work, see section 4.2.1.

Chapter 3

The [H,C,N] System, its Spectrum and Existing Data.

The infrared spectrum of the HCN/HNC system has been the subject of numerous theoretical [116, 131, 133] and experimental [84, 125, 126, 147] studies and continues to be of great interest to both molecular spectroscopy and astronomy (see chapter 1). Within molecular spectroscopy the HCN/HNC system is a prototypical isomerising molecule with stable (HCN) and a metastable (HNC) isomers both with linear geometries. The H nucleus in the bending mode of the molecule undergoes large amplitude motion, so much so that high excitation can result in the H nucleus becoming delocalised and can provide an isomerisation pathway.

3.1 Vibrational and Rotational Motion.

All molecules can undergo three types of nuclear motion. These are: translation, vibration and rotation. This work is concerned with the internal vibrational motion of the molecule. That is, the rotational and vibrational motion. Molecules have $3N - 3$ internal degrees of freedom, N being the number of nuclei. The internal degrees of freedom of linear HCN and HNC are: two stretching vibrational modes, a doubly degenerate bending vibrational mode and a doubly degenerate rotational mode.

The four vibrational modes are illustrated in figure 3.1. These vibrational modes are identified by the approximate quantum numbers v_1 , v_2 and v_3 .

v_1 is H to C stretch (or H to N stretch for HNC), which can take any positive integer value or zero.

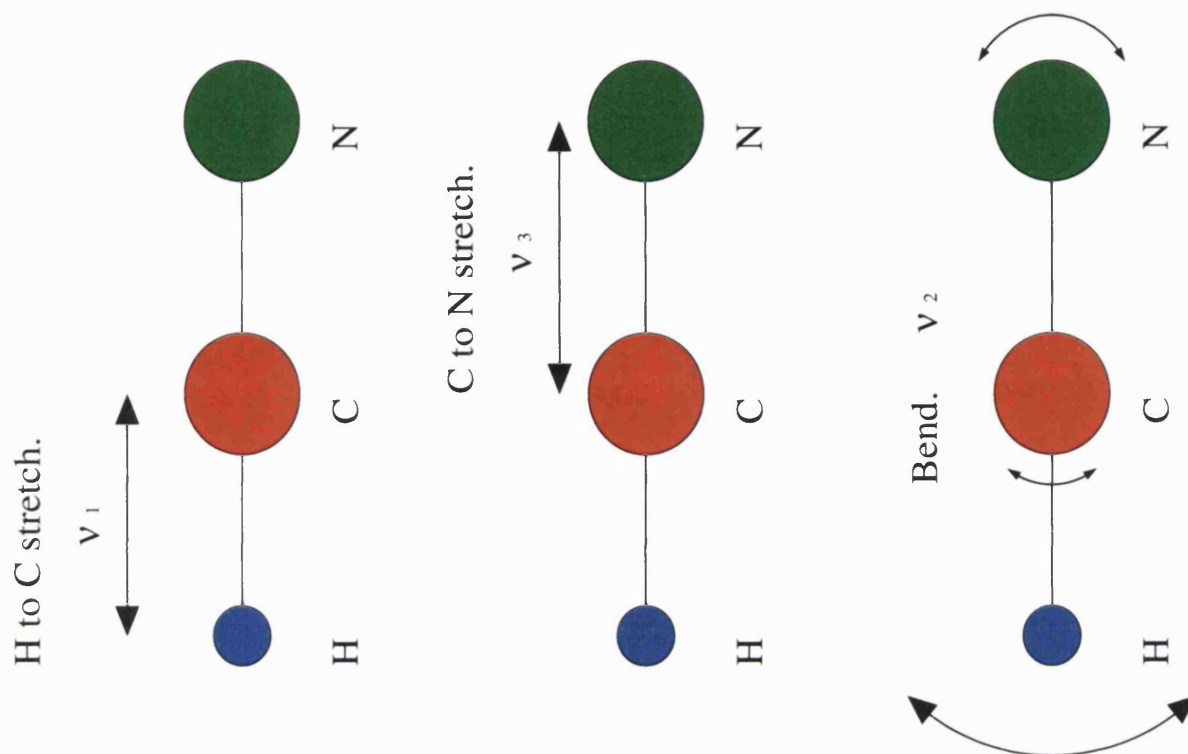


Figure 3.1: The 4 vibrational modes of HCN.

v_2 is degenerate bend, which can take any positive integer value or zero. This mode is degenerate as the molecule can bend in two planes. For example in the plane of the page or out of the plane of the page.

v_3 is the C to N stretching mode, which can take any positive integer value or zero.

Linear HCN can rotate in two equivalent orthogonal planes, again for example in the plane of the page and out of the plane of the page. The total angular momentum quantum number, J , can take any positive integer value or zero. Total angular momentum, J , is a rigorous quantum number. For each J level there are $2J + 1$ sublevels. These are the number of orientations the angular momentum can take in a magnetic field. A rotational state has even parity for an even value of J and odd parity for odd value of J , which can be expressed by $(-1)^J$.

Associated with the degenerate v_2 mode is l the vibrational angular momentum, which can take integer values in steps of 2 of $l = v_2, v_2 - 2, \dots, 2 - v_2, -v_2$. As the vibrational angular momentum, l , is part of the total angular momentum, l cannot take a value greater than J , i.e. $l \leq J$. The vibrational angular momentum can be thought of as a superposition of the vibrations in the two orthogonal planes. This results in a circular or elliptical vibrational motion, clearly this is a deviation from full linearity. Throughout

this work vibrational states are labeled as $(v_1, v_2, l^e \text{ or } f, v_3)$.

The states with $\pm l$ have almost the same energy and would be degenerate, were it not for l -type doubling, which splits states with $\pm l$, see below. In keeping with the convention of Brown *et al* [157] $\pm l$ states are labeled e or f . Where e is the lower energy state and f is the higher energy state. The e states have the same parity as the $l = 0$ states and the f states are of opposite parity. As a consequence e states have a parity of $(-1)^J$ and f states have a parity of $(-1)^{J+1}$. Parity is a “rigorous” quantum number. States with $l = 0$ are referred to as Σ states, likewise $l = 1$ states are Π states and $l = 2$ states are Δ states and so on.

3.1.1 Rotational Constants.

The eigenvalues of a linear polyatomic rigid rotor are:

$$E_r = B[J(J+1) - l^2] \quad (3.1)$$

here B is the rotational constant which is given by:

$$B = \frac{h}{8\pi^2 I c} \quad (3.2)$$

where I is the moment of inertia of the molecule, c is the speed of light and h is Planck's constant. Clearly a real molecule is not rigid, but becomes distorted as the molecule rotates and vibrates. To try to account for centrifugal distortion and other distortions further terms are added to equation 3.1, For example:

$$E_r = B[J(J+1) - l^2] - D[J(J+1) - l^2]^2 + H[J(J+1) - l^2]^3 \quad (3.3)$$

where B and D are the rotational and centrifugal distortion constants respectively and H is the sextic distortion constant which is often omitted. However this polynomial remains approximate representation of a real molecule and breaks down for high J . It is common that experimentalists [139, 138] fit their experimentally determined rovibrational energy levels using an equation of the form:

$$E(v, l, J) = G_{vl} + B_v[J(J+1) - l^2] - D_v[J(J+1) - l^2]^2 + H_v[J(J+1) - l^2]^3 + F_{vl}(J) \quad (3.4)$$

where $E(v, J)$ is the energy of the rotational vibrational state, G_{vl} is the vibrational energy, B_v and D_v are the rotational and centrifugal distortion constants respectively for a given vibrational state. Here $F_{vl}(J)$ is a further polynomial included, for example, by Burkholder *et al* [139] to account for l -type doubling in HNC. l -type doubling is the splitting of the

$l > 0$, $\pm l$ states into two non-degenerate states. l -type doubling is a consequence of the break down in the linearity of the molecule, in which the molecule becomes, slightly, an asymmetric top. Where the quantum number l is identical to the quantum number k used for asymmetric top molecules. The degree of l -type doubling is determined from the off-diagonal matrix elements $\langle v_1, v_2, v_3, \mp l, J | H | v_1, v_2, v_3, \pm l, J \rangle$, for example for $l = 1$ and $v_2 = 1$:

$$\begin{aligned} F_{vl}(J) &= \pm \frac{1}{2} [\langle v_1, v_2 = 1, v_3, l = 1, J | H | v_1, v_2 = 1, v_3, l = -1, J \rangle \\ &\quad + \langle v_1, v_2 = 1, v_3, l = -1, J | H | v_1, v_2 = 1, v_3, l = 1, J \rangle] \\ &\approx \pm \frac{1}{2} J(J+1) [q_v - q_v^J J(J+1)] \end{aligned} \quad (3.5)$$

where q_v is the l -doubling constant and q_v^J is a further centrifugal distortion constant. States with $l > 1$ can also become split. The off-diagonal terms that are responsible for l -type doubling become further off diagonal as l increases. As a result the magnitude of l -type splitting decreases with increasing l . Note also that $l = 0$ states are non-degenerate, so cannot be split and $F_{v0}(J) = 0$.

l -type doubling is a special case of l -type resonance which is the coupling between levels which have the same quantum numbers except l . l -type resonance/doubling arises from the interaction of the vibrational motion with the rotational motion, illustrating that the vibrational and rotational motion is not fully separable. The non-vanishing off-diagonal matrix elements $\langle v_1, v_2, v_3, l, J | H | v_1, v_2, v_3, l \pm 2, J \rangle$ and for higher order terms $\langle v_1, v_2, v_3, l, J | H | v_1, v_2, v_3, l \pm 4, J \rangle$ derived by Watson [170] have been used by Maki *et al* [138, 147] to account for l -type resonance in HCN. Maki *et al* [138, 147] experimentally determined the constants of l -type doubling. The magnitude of the quadratic l -type doubling/resonance constant q_v in the results of Maki *et al* is typically, about 10^{-3} cm^{-1} three orders of magnitude smaller than the quadratic rotational constant B_v . Clearly l -type doubling/resonance are relatively small effects.

The rotational constants can be used to estimate the level populations of rotational energy levels at a given temperature. This is useful when deciding to what level of rotational excitation the calculation of the linelist must extend. An approximate expression for the population of a rotational level J , relative to the ground state ($J = 0$), can be obtained from equation 3.1 combined with the Boltzmann equation and rotational degeneracy:

$$\frac{P(J)}{P(0)} = (2J+1) \exp \left(\frac{-BJ(J+1)}{kT} \right) \quad (3.6)$$

where $P(J)$ is the probability of a given molecule occupying the rotational state J , $P(0)$

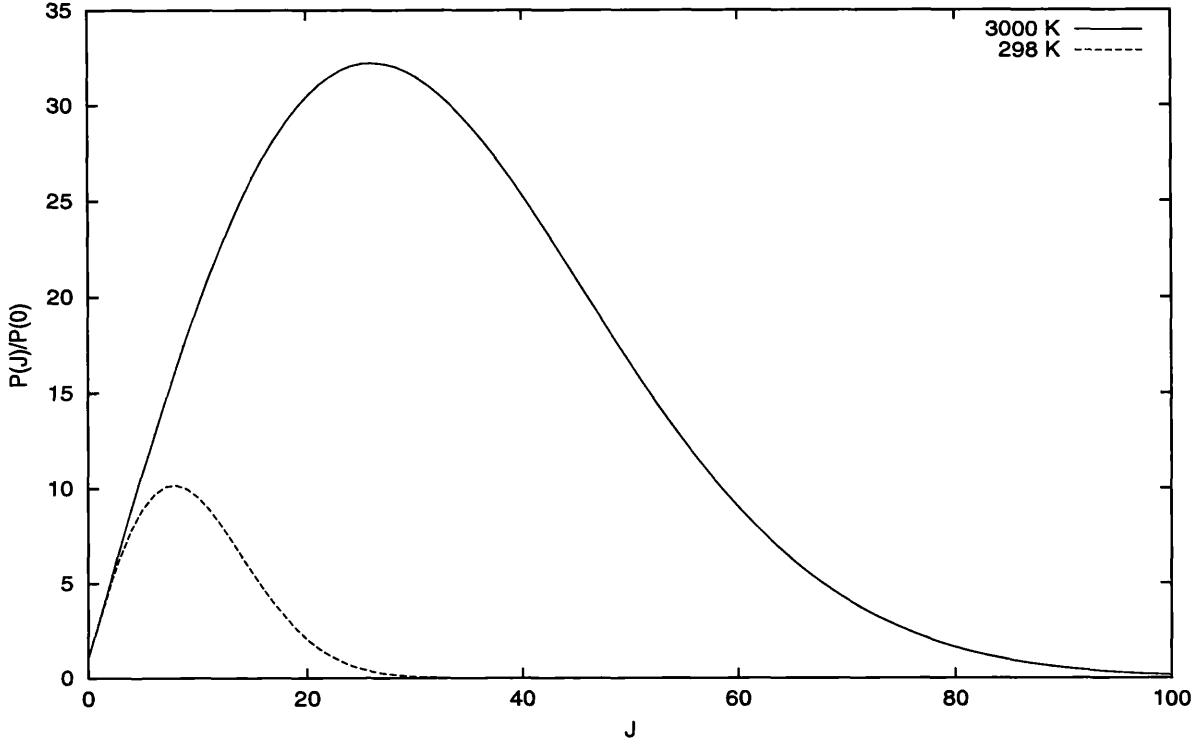


Figure 3.2: A plot of equation 3.6 illustrating the population of a given rotational level, J , relative to the population of the ground state at $T=3000$ K and $T=298$ K.

is the probability of a molecule occupying the ground rotational state, B is the rotational constant, T is temperature and k is Boltzmann's constant. Here the quartic and higher rotational terms have been neglected. Figure 3.1.1 shows a plot of this function at $T=298$ K. The maximum of equation 3.6 as a function of temperature can be determined by differentiating with respect to J and equating to zero to obtain:

$$J_{max} = \frac{1}{2} \left[\sqrt{\frac{2kT}{B}} - 1 \right] \quad (3.7)$$

From the observed HCN ground vibrational state rotational spectrum Maiwald *et al* [111] have determined value of $B = 1.47822 \text{ cm}^{-1}$. Using this value of B with equation 3.7 at $T = 298$ K, the most populated rotational level is at $J = 8$. At $T = 3000$ K, the highest stellar temperature at which HCN is observed, the most populated level is $J = 26$.

3.1.2 Selection Rules

The dipole selection rules for a harmonic oscillator allow only a change in the vibrational quantum number of 1 or zero, ie $\Delta v = \pm 1$ or $\Delta v = 0$. However the real HCN and HNC

molecules are anharmonic, therefore the dipole selection rules become:

$$\Delta v = \text{any}, \Delta J = 0, \pm 1, \Delta l = 0 \quad (3.8)$$

with $\Delta J = 0$ not allowed if $l = 0$. And:

$$\Delta v = \text{any}, \Delta J = 0, \pm 1, \Delta l = \pm 1 \quad (3.9)$$

Transitions with $\Delta l = 0$ are called parallel transitions on account that they arise from the component of the dipole moment along the axis of the molecule. Likewise $\Delta l = \pm 1$ transitions are called perpendicular transitions on account that they arise from the component of the dipole perpendicular to the axis of the molecule.

Some bending states with different orbital angular momentum (l) can become coupled by Coriolis interactions, resulting in l being poorly defined. In this event the selection rules on l are not rigidly obeyed. An example of this is the $(00^0 0) \rightarrow (02^2 0)$ transition, a dipole forbidden transition, see chapter 6.

In this work the transition dipole of all the transitions that are not rigorously forbidden are calculated. These transitions are defined only by selection rules applying to the rigorous quantum numbers J and parity. The rigorous selection rules require a change in overall parity and that $|\Delta J| \leq 1$. The transitions that are calculated in this work are therefore:

$$\Delta J = \pm 1, e \rightarrow e \text{ or } f \rightarrow f \quad (3.10)$$

$$\Delta J = 0 e \rightarrow f \text{ or } f \rightarrow e \quad (3.11)$$

These rules allow the calculation of the transition dipole of 'forbidden' transitions, such as the $00^0 0 \rightarrow 02^2 0$ where $\Delta l > 1$, see chapter 6.

3.2 Intensity Factors

It is common for experimentalists to reduce their measured line intensities to band intensities or band transition dipoles. This is usually done by implementing Hönl–London [99] factors. Hönl–London factors give the intensity of a line relative to the lines with $J' = 0$ or $J'' = 0$. By using these Hönl–London factors the intensities of individual lines can be reduced to a single band intensity which represents the intensity of a band. Maki *et al* [125] also use vibrational intensity factors. Maki *et al* [125] derived these vibration intensity factors based upon the earlier derivation of Wilson *et al* [171]. The vibrational intensity factors give the relative band intensity of a hot band to its respective cold band.

To ease comparison with experiment the line intensities calculated in this work are reduced to band transition dipoles. The band transition dipole is related to the transition dipole strengths of an individual rotational vibrational line of a band by:

$$\mu_l = \mu_b \sqrt{F_{HL}(J, l) F_v(v_1, v_2, l, v_3)} \quad (3.12)$$

where μ_b and μ_l are the band and line transition dipoles respectively, F_{HL} and F_v are the Hönl–London and vibrational intensity factors respectively. The Hönl–London factors are the rotational intensity factors. They give the intensity of a line in a band relative to the intensity of the pure vibrational transition for a rigid rotor. So by factorising rotational and vibrational components we obtain:

$$\langle v'_1, v'_2, l', v'_3, J' | \mu | v''_1, v''_2, l'', v''_3, J'' \rangle = \langle v'_1, v'_2, l', v'_3 | \mu | v''_1, v''_2, l'', v''_3 \rangle \sqrt{F_{HL}(J'', l'')} \quad (3.13)$$

The vibrational intensity factors are obtained using a harmonic oscillator representation for each of the 4 vibrational modes. They give the intensity of a vibrational transition relative to the vibrational transition to the ground state or lowest possible state, with the same change in quantum numbers. For example:

$$\begin{aligned} \langle v_1 + \Delta v_1, v_2 + \Delta v_2, l + \Delta l, v_3 + \Delta v_3 | \mu | v_1, v_2, l, v_3 \rangle &= \langle \Delta v_3, \Delta v_2, \Delta l, \Delta v_3 | \mu | 0, 0, 0, 0 \rangle \\ &\times \sqrt{F_v(v_1, v_2, l, v_3)} \end{aligned} \quad (3.14)$$

By combining equations 3.14 and 3.13 equation 3.12 is acquired. The band dipole for bands which have the same change of vibrational quantum number are approximately equal. The real HCN/HNC molecule is not a rigid rotor or a harmonic oscillator so both the Hönl–London and vibrational intensity factor are approximate and often unrealistic representations.

To correct for the inapplicability of the rigid rotor approximation, a further factor, the Herman-Wallis function is sometimes included in equation 3.12. Maki *et al* [125], for HCN, use a Herman-Wallis function for Q branch transitions of:

$$F^Q = [1 + A_2^Q J(J+1) + A_4^Q \{J(J+1)\}^2]^2 \quad (3.15)$$

and for P and R branch transitions:

$$F^{PR} = [1 + A_1^{PR} m + A_2^{PR} m^2]^2 \quad (3.16)$$

where A_n are the Herman-Wallis constants and m takes the value of $-J''$ for P branch transitions and of $J'' + 1$ for R branch transitions. Most bands have a Hönl–London like

intensity structure which results in small Herman-Wallis constants of the order of 10^{-4} , for example see Maki *et al* [125]. For these bands the Herman-Wallis function has little effect until high J . However for bands with unusual intensity structure such as the HCN CN stretch fundamental, see section 6.2.1 and figure 6.4, the effect of the Herman-Wallis function is much larger. The Herman-Wallis constants give empirical representation of the intensity structure of the band. It is therefore more meaningful to give the line transition dipoles rather than fitting Herman-Wallis functions. Therefore for bands with unusual intensity structure the line transition dipoles or intensities will be given directly.

The vibrational intensity factors are derived by Maki *et al* [125] by expanding the dipole in a Taylor series and using harmonic oscillator functions for the vibrational wave functions. The vibrational intensity factor for the non-degenerate stretching vibrations is different from that of the doubly degenerated bend. As a result, for HCN, the vibrational intensity factor is factorised into degenerate and non-degenerate parts: $F_v = L_{13}L_2$ where L_{13} is the non-degenerate part for the stretching vibrations and L_2 is the degenerate part for the bending vibration. Maki *et al* [125] used the following expressions for L_{13} and L_2 :

$$L_{13} = \frac{(v_1 + \Delta v_1)!(v_3 + \Delta v_3)!}{v_1!v_3!\Delta v_1!\Delta v_2!} \quad (3.17)$$

For parallel bands (Δl even) L_2 takes the form:

$$L_2 = \frac{[\frac{1}{2}(v_2 + l + \Delta v_2)]![\frac{1}{2}(v_2 - l + \Delta v_2)]!}{[\frac{1}{2}(v_2 + l)]![\frac{1}{2}(v_2 - l)]![\frac{1}{2}\Delta v_2!]^2} \quad (3.18)$$

and for perpendicular bands (Δl odd) L_2 takes the form:

$$L_2 = \frac{[\frac{1}{2}(v_2 + l + \Delta v_2 - 1)]![\frac{1}{2}(v_2 - l + \Delta v_2 - 1)]![v_2 + l\Delta l + \Delta v_2 + 1]}{g_v[\frac{1}{2}(v_2 + l)]![\frac{1}{2}(v_2 + l)]![\frac{1}{2}(v_2 + l)]!\{[\frac{1}{2}(\Delta v_2 - 1)]!\}^2[\Delta v_2 + 1]} \quad (3.19)$$

In the above equations v_1 , v_2 and v_3 all take the smaller value of the upper or lower state values. Δv_1 , Δv_2 and Δv_3 are always positive. If $v_2 = v'_2$ then $l = l'$ and $\Delta l = l'' - l'$, otherwise $l = l''$ and $\Delta l = l' - l''$. $g_v = 1$ if l' or l'' equal 0, otherwise $g_v = 2$. The g_v factor is included to account for the fact that both $e \rightarrow f$ and $f \rightarrow e$ transitions are possible when $l' > 0$ and $l'' > 0$. Only one of these blocks of transitions are possible if $l' = 0$ or $l'' = 0$.

As mentioned many times these intensity factors are only approximate. They are used in this work only to ease the comparison of the *ab initio* lines with experiment. In fact Hönl-London factors do not reproduce unusual rotation dependent intensity structure, such as that of the HCN CN stretch fundamental and also the intensity borrowing phenomena (see chap 6).

3.2.1 Derivation of Hönl–London Factors.

In the published experimental work on HCN, two groups, those of Maki and co-workers [125] and Smith and co-workers [126] use different Hönl–London factors. Smith *et al* [126] use Hönl–London factors that are a factor of 4 and 2 greater than those of Maki *et al* [125] for the $\Pi - \Sigma$ and $\Sigma - \Pi$ bands, respectively. This in turn will give band dipoles that are a factor of $\frac{1}{2}$ and $\frac{1}{\sqrt{2}}$ the band dipole's calculated with the Hönl–London factors used by Maki *et al*, for the $\Pi - \Sigma$ and $\Sigma - \Pi$ bands, respectively. To compare *ab initio* and experimental dipole band strengths it is necessary to know which Hönl–London factor was used to calculate the experimental dipole band strength and use the same factor to calculate the *ab initio* band dipole. In this work we employ the Hönl–London factors used by Maki *et al* which we re-derive from the matrix elements given by Gordy and Cook [127].

Rotational transitions can be thought of as being induced by the interaction of the electromagnetic field of the radiation, which is fixed in space co-ordinates, with the electric dipole which is fixed in body fixed co-ordinates. The electric dipole of a linear molecule lies directly along the axis of rotation it is therefore clearly not fixed in spacial co-ordinates. A transformation to space fixed is thus required.

X, Y, Z are chosen to represent the space fixed normal axes, denoted in general as F where $F = X, Y, Z$. x, y, z are chosen to represent the body fixed normal axes, denoted in general as g where $g = x, y, z$, with z axis along the C-N bond. The component of the dipole along the space fixed F axis is given by:

$$\tilde{\mu}_F = \mu_x \Phi_{Fx} + \mu_y \Phi_{Fy} + \mu_z \Phi_{Fz} \quad (3.20)$$

where $\tilde{\mu}_F$ are the components of the dipole moment in space fixed co-ordinates and μ_g are the components of the dipole moment in the body fixed co-ordinates. The Φ_{Fg} is the cosines of the angle between the F space fixed and g body fixed axis. The component of the transition dipole or matrix element along the space fixed F axis is given by:

$$\begin{aligned} \langle J, l | \tilde{\mu}_F | J', l' \rangle &= \mu_x \langle J, l | \Phi_{Fx} | J', l' \rangle + \mu_y \langle J, l | \Phi_{Fy} | J', l' \rangle + \mu_z \langle J, l | \Phi_{Fz} | J', l' \rangle \\ &= \sum_g \mu_g \langle J, l | \Phi_{Fg} | J', l' \rangle \end{aligned} \quad (3.21)$$

We therefore require the matrix elements of all 9 direction cosine elements. Gordy and Cook [127] give the factors of the direction cosine elements for symmetric tops, which are quoted in table 3.1. The following discussion uses these previously derived matrix elements

to derive Hönl–London factors. The linear molecule is a special case of the symmetric top, for which the quantum number l is identical to k though the definitions are slightly different. l is the vibrational angular momentum and k represents the projection of the angular momentum onto the body fixed z axis. In this discussion we use the notation of Gordy and Cook [127], where $k = K$ and a further quantum number M is introduced. M is the projection of the angular momentum onto the space fixed Z axis.

Table 3.1: Factors of Direction Cosine Matrix Elements of Symmetric Top Rotors. This table is taken from Gordy and Cook [127] pg 32.

Matrix Element Factor	Value of J'		
	J+1	J	J-1
$\langle J \Phi_{Fg} J' \rangle$	$\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}$	$[4J(J+1)]^{-1}$	$[4J(4J^2-1)^{1/2}]^{-1}$
$\langle J, K \Phi_{Fz} J', K \rangle$	$2[(J+1)^2 - K^2]^{1/2}$	$2K$	$-2(J^2 - K^2)^{1/2}$
$\langle J, K \Phi_{Fy} J', K \pm 1 \rangle = \mp i \langle J, K \Phi_{Fx} J', K \pm 1 \rangle$	$\mp [(J \pm K + 1)(J \pm K + 2)]^{1/2}$	$[J(J+1) - K(K \pm 1)]^{1/2}$	$\mp [(J \mp K)(J \mp K - 1)]^{1/2}$
$\langle J, M \Phi_{Zg} J', M \rangle$	$2[(J+1)^2 - M^2]^{1/2}$	$2M$	$-2(J^2 - M^2)^{1/2}$
$\langle J, M \Phi_{Yg} J', M \pm 1 \rangle = \pm i \langle J, M \Phi_{Xg} J', M \pm 1 \rangle$	$\mp [(J \pm M + 1)(J \pm M + 2)]^{1/2}$	$[J(J+1) - M(M \pm 1)]^{1/2}$	$\mp [(J \mp M)(J \mp M - 1)]^{1/2}$

The direction cosine matrix elements can be found from the factors of the direction cosine matrix elements in table 3.1, by:

$$\langle J, K, M | \Phi_{Fg} | J', K', M' \rangle = \langle J | \Phi_{Fg} | J' \rangle \langle J, K | \Phi_{Fg} | J', K' \rangle \langle J, M | \Phi_{Fg} | J', M' \rangle \quad (3.22)$$

To find the contribution to the Hönl-London factor we must sum the squares of the space fixed matrix elements over all co-ordinates and also sum over $\Delta M = -1$ to $\Delta M = 1$, for example:

$$\mu^2 = \sum_F \sum_{\Delta M=-1}^1 \langle J, K, M | \tilde{\mu}_F | J', K', M + \Delta M \rangle \langle J, K, M | \tilde{\mu}_F | J', K', M + \Delta M \rangle^* \quad (3.23)$$

where μ is the transition dipole, and $\langle J, K, M | \tilde{\mu}_F | J', K', M + \Delta M \rangle^*$ is the complex conjugate of $\langle J, K, M | \tilde{\mu}_F | J', K', M + \Delta M \rangle$.

Consider the parallel P branch transitions which have $\Delta J = -1$ and $\Delta K = 0$. The parallel transitions are dependent in the component of the dipole that lies along the z axis. As a consequence the matrix elements in the x and y directions for $\Delta K = 0$ transitions are zero. So using equation 3.22 with table 3.1 the X, Y and Z components are:

$$\langle J, K, M | \tilde{\mu}_X | J - 1, K, M \pm 1 \rangle = \frac{-2i[(J^2 - K^2)(J \mp M)(J \mp M - 1)]^{1/2}}{4J(4J^2 - 1)^{1/2}} \mu_z \quad (3.24)$$

$$\langle J, K, M | \tilde{\mu}_Y | J - 1, K, M \pm 1 \rangle = \frac{\pm 2[(J^2 - K^2)(J \mp M)(J \mp M - 1)]^{1/2}}{4J(4J^2 - 1)^{1/2}} \mu_z \quad (3.25)$$

$$\langle J, K, M | \tilde{\mu}_Z | J - 1, K, M \rangle = \frac{4[(J^2 - K^2)(J^2 - M^2)]^{1/2}}{4J(4J^2 - 1)^{1/2}} \mu_z \quad (3.26)$$

By squaring and summing equations 3.24, 3.25 and 3.26 via equation 3.23 and multiplying by the rotational degeneracy factor of $2J + 1$ we arrive at:

$$\begin{aligned} \mu_l^2 &= \mu_z^2 \frac{(J^2 - K^2)(2J - 1)(2J + 1)}{J(4J^2 - 1)} \\ &= \mu^2 \frac{J^2 - K^2}{J} \end{aligned} \quad (3.27)$$

here μ_z is replaced by μ the band transition dipole and importantly the dependence upon M has vanished. By the same process for the parallel Q branch ($\Delta J = 0$ and $\Delta K = 0$) one obtains:

$$\mu_l^2 = \mu^2 \frac{K^2(2J + 1)}{J(J + 1)} \quad (3.28)$$

Finally for the parallel R branch ($\Delta J = +1$ and $\Delta K = 0$):

$$\begin{aligned} \mu_l^2 &= \mu^2 \frac{[(J + 1)^2 - K^2](2J + 1)}{(J + 1)(2J + 1)} \\ &= \mu^2 \frac{(J + 1)^2 - K^2}{J + 1} \end{aligned} \quad (3.29)$$

The three Hönl–London factors in equations 3.27, 3.28 and 3.29 agree with both Maki *et al* [125] and Smith *et al* [126].

The perpendicular transitions ($\Delta K \pm 1$) arise from the dipole in the body fixed xy plane. The dipole moment for linear HCN lies entirely in the z axis. However if the molecule is slightly bent there is a component of the dipole in the xy plane, allowing perpendicular transitions. The Hönl–London factors for the parallel bands are more complicated to derive from the cosine matrix elements as they have both an x and a y component. For $\Delta J = +1$ and $\Delta K \pm 1$ from the matrix element factors in table 3.1 the Z component is:

$$\begin{aligned} \langle J, K, M | \tilde{\mu}_Z | J+1, K \pm 1, M \rangle &= -\mu_y \Delta K \frac{[(J + K \Delta K + 1)(J + K \Delta K + 2)]^{1/2}}{2(J+1)[(2J+1)(2J+3)]^{1/2}} \\ &\quad \times [(J+1)^2 - M^2]^{1/2} \\ &\quad - i\mu_x \frac{[(J + K \Delta K + 1)(J + K \Delta K + 2)]^{1/2}}{2(J+1)[(2J+1)(2J+3)]^{1/2}} \\ &\quad \times [(J+1)^2 - M^2]^{1/2} \end{aligned} \quad (3.30)$$

$$\begin{aligned} &= \frac{[(J + K \Delta K + 1)(J + K \Delta K + 2)]^{1/2}}{2(J+1)[(2J+1)(2J+3)]^{1/2}} \\ &\quad \times [(J+1)^2 - M^2]^{1/2} (-\mu_y \Delta K - i\mu_x) \end{aligned} \quad (3.31)$$

here the real term is the y component and the imaginary term is the x component. Likewise the Y component is:

$$\begin{aligned} \langle J, K, M | \tilde{\mu}_Y | J+1, K \pm 1, M \pm 1 \rangle &= \frac{[(J + K \Delta K + 1)(J + K \Delta K + 2)]^{1/2}}{4(J+1)[(2J+1)(2J+3)]^{1/2}} \\ &\quad \times [(J + M \Delta M + 1)(J + M \Delta M + 2)]^{1/2} \\ &\quad \times (\mu_y + i\Delta M \mu_x) \end{aligned} \quad (3.32)$$

here ΔM can take values of $\Delta M = \pm 1$, likewise the ΔK can take values of $\Delta K = \pm 1$.

Finally the X component is:

$$\begin{aligned} \langle J, K, M | \tilde{\mu}_X | J+1, K \pm 1, M \pm 1 \rangle &= \frac{[(J + K \Delta K + 1)(J + K \Delta K + 2)]^{1/2}}{4(J+1)[(2J+1)(2J+3)]^{1/2}} \\ &\quad \times [(J + M \Delta M + 1)(J + M \Delta M + 2)]^{1/2} \\ &\quad \times (\mu_x - i\Delta K \mu_y) \end{aligned} \quad (3.33)$$

Squaring and summing the components over X, Y, Z and ΔM via equation 3.23 and multiplying by the rotational degeneracy $(2J+1)$ the following expression is obtained:

$$\begin{aligned} \mu_l^2 &= (\mu_x^2 + \mu_y^2) \frac{(J \pm K + 1)(J \pm K + 2)(2J+1)}{4(J+1)(2J+1)} \\ &= \mu^2 \frac{(J \pm K + 1)(J \pm K + 2)}{4(J+1)} \end{aligned} \quad (3.34)$$

Table 3.2: The Hönl–London factors used in this work. Where $J = J''$, $l = l''$, $\Delta J = J' - J''$ and $\Delta l = l' - l''$.

Δl	Value of ΔJ		
	+1	0	-1
+1	$\frac{(J+l+1)(J+l+2)}{2(J+1)}$	$\frac{(J(J+1)-l(l+1))(2J+1)}{2J(J+1)}$	$\frac{(J-l)(J-l-1)}{2J}$
0	$\frac{(J+1)^2-l^2}{J+1}$	$\frac{l^2(2J+1)}{J(J+1)}$	$\frac{J^2-l^2}{J}$
-1	$\frac{(J-l+1)(J-l+2)}{2(J+1)}$	$\frac{(J(J+1)-l(l-1))(2J+1)}{2J(J+1)}$	$\frac{(J+l)(J+l-1)}{2J}$

here the factor $(\mu_x^2 + \mu_y^2) = \mu^2$ is the band transition dipole and for these transitions it lies entirely in the body fixed xy axis. Taking the factors of the matrix elements all following the same procedure for the $\Delta K = \pm 1$ and $\Delta J = 0$ perpendicular Q branch transitions one obtains:

$$\mu_l^2 = \mu^2 \frac{(J(J+1) - K(K \pm 1))(2J+1)}{4J(J+1)} \quad (3.35)$$

Finally for the perpendicular $\Delta J = -1$ transitions one obtains:

$$\mu_l^2 = \mu^2 \frac{(J \mp K)(J \mp K - 1)}{4J} \quad (3.36)$$

The perpendicular Hönl–London factors given in Equations 3.34, 3.35 and 3.36 must be multiplied by 2 for transitions which have $l' = 0$ or l'' . This is because the $l = 0$ states are non-degenerate so that only one P,Q and R branch exist. The allowed P and R branch transitions have $l = 1e \rightarrow l = 0e$ and the allowed Q branch transitions have $l = 1f \rightarrow l = 0e$. Maki *et al* [125] account for this further factor of 2 as part of their vibrational intensity factors, we will follow their lead. In the work of Maki *et al* [128] the factor g_v in the bending mode's vibrational intensity factor given in equation 3.19, accounts for the non-degeneracy of the $l = 0$ states.

The final Hönl–London factors are summarised in table 3.2, where K has been replaced with l . All the perpendicular Hönl–London factors agree with Maki *et al* [125] and differ from those used by Smith *et al* [126] a factor of 4 and 2 for the $\Pi - \Sigma$ and $\Sigma - \Pi$ bands, respectively. The Hönl–London factors given by Maki *et al* [125] will be used throughout this work.

One final test remains, the intensity factors for the P, Q and R branches of a given band should sum to $2J + 1$, the rotational degeneracy. This the factors in table 3.2 all do.

3.3 Intensity Units

There are many units used by both theoreticians and experimentalists to indicate the strength of a transition. In this section I will give relations between transition dipole in Debye, line strength in Debye², integrated absorption intensity in cm⁻²am⁻¹, integrated band intensity in cm mol⁻¹ and the Einstein A coefficient. These are intensity units commonly used by the HCN experimental workers and astronomers. I will also give a brief description of how these intensities are linked to the opacity function or the monochromatic absorption coefficient κ_ν or κ_λ , discussed in section 1.3.

If we consider a beam of radiation, with intensity $I_{0\nu}$, passing through a gas with path length l pressure p and a HCN mixing ratio of x . Then neglecting emission from the gas and absorption from anything other than HCN/HNC, a solution to equation 1.13, is:

$$I_\nu = I_{0\nu} \exp(-\kappa_\nu p x l) \quad (3.37)$$

where I_ν is the detected intensity. Equation 3.37 is called the Lambert-Beer law. It follows from this that in this case the units of κ_ν are 1/($p x l$), often chosen by experimentalists as cm⁻¹ atm⁻¹. The integrated absorption intensity S_i of line i , is the integral of κ_ν over all frequencies, so it follows that:

$$\begin{aligned} S_i &= \int_{-\infty}^{+\infty} \kappa_\nu d\nu \\ &= \frac{1}{p l} \int_{-\infty}^{+\infty} \ln \left(\frac{I_0}{I} \right)_\nu d\nu \end{aligned} \quad (3.38)$$

This line intensity is the quantity usually given by experimentalists, it related to line strength and band transition dipole by:

$$S_i = \frac{2\pi^2 L \nu}{3 h c \epsilon_0 Q_{vr}} \left(\frac{273.15}{T} \right) \exp \left(\frac{-E''}{kT} \right) \left[1 - \exp \left(\frac{-h c \nu}{kT} \right) \right] S(f - i) \quad (3.39)$$

$$\approx \frac{2\pi^2 L \nu}{3 h c \epsilon_0 Q_{vr}} \left(\frac{273.15}{T} \right) \exp \left(\frac{-E''}{kT} \right) \left[1 - \exp \left(\frac{-h c \nu}{kT} \right) \right] F_{HL} F_v R_B^2 \quad (3.40)$$

here, for clarity we use SI units where possible, S_i is line intensity (m⁻² atm⁻¹), L is Loschmidt's number (2.686763×10^{25} molecules m⁻³ at 1 atm and 273.15 K), ν is the wavenumber in m⁻¹ of the line, h is Planck's constant, c is the speed of light, ϵ_0 is the permittivity of free space, k is Boltzmann's constant, E'' is the energy of the lower ro-vibrational energy level, T is the temperature, Q_{vr} is the ro-vibrational partition function and $S(f - i)$ is the line strength in (Coulomb meters)² and R_B is the band transition dipole in Coulomb meters (1 Debye = 3.33564×10^{-30} C m). Finally F_{HL} and F_v are

the Hönl–London and vibrational intensity factors respectively, see section 3.2. The line strength $S(f-i)$ is calculated by the DIPOLE3 code, see section 2.7.3. $S(f-i)$ is related to the line transition dipole R_l by $S(f-i) = (2J''+1)R_l^2$. For the particular combination of units of dipole moment in Debye, absolute intensity in $\text{cm}^{-2} \text{ atm}^{-1}$ and wavenumber in cm^{-1} , equation 3.39 becomes:

$$S_i = \frac{11.183309 \times \nu}{Q_{vr}} \left(\frac{273.15}{T} \right) \exp \left(\frac{-E''}{kT} \right) \left[1 - \exp \left(\frac{-hc\nu}{kT} \right) \right] S(f-i) \quad (3.41)$$

The factor in square brackets on the RHS of eq. 3.41 is the population difference between the two states, which gives rise to induced emission. The factor $\exp \left(\frac{-E''}{kT} \right)$ is proportional to the population of the lower state energy.

To convert from intensity in $\text{cm}^{-2} \text{ atm}^{-1}$, to band intensity in the units used by Smith *et al* [126] of cm mol^{-1} , one must use the following equation:

$$I_B(\text{cm mol}^{-1}) = S_i(\text{cm}^{-2} \text{ atm}^{-1}) \frac{Q_{vr} N_A}{L} \frac{T}{273.15} \exp \left(-\frac{E''}{kT} \right) F_{HL} F_v \quad (3.42)$$

where N_A is Avogadro's number and I_B is the band intensity. In this work a value of $Q_{vr}(298 \text{ K}) = 149.944$ given by Maki *et al* [137] was used.

The experimental data of Smith *et al* [83, 126, 129, 130] and the earlier theoretical work of Botschwina and co-workers [131, 132, 133], was originally reported as integrated band intensities (cm mol^{-1}). For consistency we have converted these band intensities to band transition dipole's. By using equations 3.40 and 3.42 band intensity can be related to band transition dipole by the formula:

$$I_B \approx \frac{2\pi^2 N_A \nu_0}{3hc\epsilon_0} \left[1 - \exp \left(\frac{-hc\nu_0}{kT} \right) \right] R_B^2 \quad (3.43)$$

Again for clarity we use SI units, where I_B is band intensity in m mol^{-1} , is Avogadro's number, ν_0 is the wavenumber in m^{-1} of the band center and R_B is the band transition dipole in Coulomb meters. The approximation here is a result of using the wavenumber of the band centers rather than that of the individual lines. At worst this approximation is accurate to a few percent, better than the approximation made when using Hönl–London factors and less than the experimental statistical error. The factor in square brackets on the RHS of eq. 3.43 is the population difference between the two states. It gives rise to induced emission and is very close to 1 for the range of results reported in this work. With rearrangement and using the particular combination of units of dipole moment in Debye, intensity in cm mol^{-1} and wave number in cm^{-1} , the above formula becomes:

$$R_B \approx \sqrt{\frac{I_B}{2.5066379 \times 10^5 \times \nu_0}} \quad (3.44)$$

This equation is of the same form as used by Botschwina *et al* [131], to convert between band transition dipole and band intensity.

The Einstein A_{ul} coefficient is the rate of spontaneous emission between upper state u and lower state l . The Einstein A_{ul} coefficient is often used by astronomers and is related to the transition dipole by:

$$R_{l,ul}^2 = \frac{(2J' + 1)A_{ul}}{(2J'' + 1)\nu^3} \quad (3.45)$$

A_{ul} is usually given in units of s^{-1} , note that $R_{l,ul}$ must be in units of $s^{-1/2}$.

If units of Debye² for R , cm^{-1} for frequency and S^{-1} for A are used, then the RHS of equation 3.45 must be divided by $3.136186 \times 10^{-7} s^{-1}$.

3.4 Available Experimental Data.

Much experimental work has been carried out on the rotation-vibrational spectrum of the HCN molecule throughout the last century. The published experimental work from just the last 15 years totals over 20 papers. As a result there is a huge amount of data available for HCN. Measurements of the strong ν_1 H to C stretch mode extend up to 7 quanta [130] and $23000 cm^{-1}$. Recently Picqué and Guelachvili [86] have measured an extensive series of hot bands with $\Delta\nu_1 = 1$. Several of which have not had their intensity determined. Measurements of the strong ν_2 bending and weak ν_3 stretching modes extend to 10 quanta [147] and 3 quanta respectively [83]. Transitions involving excitation in only the ν_3 mode are weak and the fundamental shows unusual intensity structure [128], which has a “double peaked” R branch, see chapter 6. However the intensity of the stretching combination overtones such as $(1, 0^0, \nu_3)$ are considerably stronger, allowing measurement up to higher excitations. For example the $(0, 0^0, 0) \rightarrow (1, 0^0, 4)$ transition was measured by Smith *et al* [126]. Pure rotational transitions of HCN have been measured by Maiwald *et al* [111] up to $J = 21 \rightarrow 22$. The data they measured allows the determination of pure rotational energy levels up to $J = 18$.

A great deal of intensity data on HCN also exists largely as a result of the measurements of Smith and co-workers [126, 83, 129, 130] and Maki and co-workers [125, 128, 137]. Most of this data has been reduced to band intensities or band dipole’s except where a band has unusual intensity structure. During the course of the works of Smith and co-workers a controversy over the intensity of the $(0, 0^0, 0) \rightarrow (5, 0^0, 1)$ band erupted. The absolute band intensity of the $(0, 0^0, 0) \rightarrow (5, 0^0, 1)$ band was measured by Smith *et al* [83] to be $13.9 cm mol^{-1}$, much stronger than the $(0, 0^0, 0) \rightarrow (6, 0^0, 0)$ band which they measured

to be 2.4 cm mol^{-1} . Botschwina [132] calculated via the *ab initio* coupled electron pair approximation (CEPA) method the intensity to be 4.3 cm mol^{-1} . This was backed up by Baggott and Law [168] who measured the intensity of the $(0,0^0,0) \rightarrow (5,0^0,1)$ band, their result agreed well with theory. Despite a re-measurement of the $(0,0^0,0) \rightarrow (5,0^0,1)$ band by Smith *et al* [129] which claimed to be the definitive result. The controversy was not resolved until 3 years later Romanini and Lehmann [130] measured the intensity to be 3.5 cm mol^{-1} a value that agrees with experiment and theory and is now the accepted value. Romanini and Lehmann [130] attributed the incorrect measurements of Smith *et al* [83, 129] to the relatively short path length of their apparatus. This may cast some doubt on the accuracy of the other measurements of Smith *et al* [83, 129]. However for the $(6,0^0,0)$ band Romanini and Lehmann [130] had good agreement with with Smith *et al* [83, 129]. Furthermore none of the other measurements performed by Smith *et al* [83] disagreed to such an extent with theory. None-the-less the measurements of Smith *et al* [83] are 13 years old. The improvements in experimental techniques over the last 13 years should yield improved measurements of the high overtones of HCN.

In contrast to HCN prior to its detection in the interstellar medium in 1971 by Snyder and Bhull [19, 20], HNC had only been observed by means of matrix isolation spectroscopy [166]. HNC proved difficult to generate and isolate in the lab. As a result the gas phase infra red absorption spectrum of HNC was not observed [103] until 10 years after the detection of HNC in the interstellar medium. Maki and Sams [103] heated pure HCN to 1200 K so that the HNC to HCN ratio at thermodynamic equilibrium was improved sufficiently to allow the measurement of the absorption spectrum of HNC. By combining their results with earlier HNC gas discharge emission measurements [169] and assuming thermodynamic equilibrium they calculated a value for the energy of the ground state of HNC relative to the ground state of HCN. More recently Northrup *et al* [150] have measured absorption spectra of HNC over the range 3225 to 3850 cm^{-1} , the region of the H to N (v_1) fundamental. They generated HNC by reaction of 'hot' H atoms with ClCN. Their frequency measurements allowed the determination of the excited H to N stretch energy levels, $(v_1, 0^0, 0)$ with $v_1 = 1, 2, 3, 4$, some stretch combination levels, $(v_1, 0^0, 1)$ states with $v_1 = 0, 1, 2$ and finally some H to N stretching levels $(v_1, 1^1, 0)$ with $v_1 = 0, 1, 2, 3$. Maki and Mellau [143] have recently measured high bend excitations of HNC via high temperature (1300 K) emission spectra. Again they heated HCN to form an equilibrium mixture of HCN and HNC. They were able to determine the energies of excited

HNC bending states up to $(0, 3^3, 0)$ and some bending and stretching combination levels, up to $(1, 5^5, 0)$ and $(0, 3^3, 1)$. Pure HNC rotational transitions up to $J = 3 \rightarrow 4$ have been measured by Okabayashi and Tanimoto [113]. Their measurements included pure rotational transitions in the first vibrationally excited states.

To date the intensities of only the HNC stretching fundamentals have been directly measured. He and Macdonald [167] determined a band transition dipole of 0.141 D for the H to N stretch fundamental. Nezu *et al* [140, 141] have measured the band transition dipole of the v_1 and v_2 fundamentals to be 0.156 D and 0.106 D respectively. The value of the v_1 fundamentals measured by He and Macdonald [167] and Nezu *et al* [140, 141] agree within experimental error. Nezu *et al* [140, 141] inferred a band transition dipole for the v_2 fundamental from those of the v_1 and v_3 fundamentals using the Herman-Wallis effect. The value of 1.04 D that they obtained for the band transition dipole of the v_2 fundamental is double the *ab initio* value calculated by Lee and Rendell [142] and the value calculated in this work, see chapter 6. This casts doubt on the empirical method that Nezu *et al* used to determine the transition dipole of the HNC bending fundamental.

3.5 Available Empirical Potential Surfaces.

Empirical potential energy surfaces (PES) are fitted to experimental data so that energy levels calculated from them reproduce as closely as possible the fitted experimental data. The first such fitted global HCN/HNC PES is that of Murrell *et al* [101]. Murrell *et al* adjusted their PES to minimise the difference between experiment and the energy levels they calculated with their PES via a variational method. HCN states with energy less than 9000 cm^{-1} were reproduced to within 2 cm^{-1} , but states above 9000 cm^{-1} in energy deviate by more than 5 cm^{-1} from experiment. The HNC stretching fundamentals are reproduced to within 3 cm^{-1} . Later Carter *et al* [135, 136] fitted a HCN only potential surface to within 0.5 cm^{-1} of ro-vibrational $J = 0, 1, 2$ levels up to 18000 cm^{-1} . Most recently Wu *et al* [119] have fitted an empirical correction for the global HCN/HNC *ab initio* potential surface of Bowman *et al* [116] to experimental data. They fitted 71 experimentally determined energy levels with energies up to 18500 cm^{-1} and with $J = 0$ and 1 to better than 0.01 cm^{-1} .

Empirical PES reproduce the fitted experimental data very well. However the fitted potential only forms a good representation of the ‘real’ PES in the regions of the potential which are ‘probed’ by the fitted experimental data. Wave functions with significant

magnitude in the ‘unprobed’ regions of the potential surface are poorly reproduced. As a result energy levels not included in the fit can be poorly reproduced and have an unpredictable deviation from the real energy. Using a good starting point such as a good *ab initio* PES can reduce this problem. The *ab initio* PES will already reproduce energy levels to a predictable accuracy and give a good approximation to the ‘real’ PES. Hence the ‘unprobed’ regions of the fitted PES have a reasonably good representation prior to fitting. The fact that the PES of Wu *et al* [119] uses the good *ab initio* PES of Bowman *et al* [116] as a starting point and fits experimental data to 0.01 cm^{-1} , means that it is by far the best available fitted HCN/HNC PES.

3.6 Available *ab initio* Surfaces and Data.

Much work on *ab initio* potential surfaces has been done. The available surfaces can be divided into three groups, 2D stretching only potentials, 3D partial PES and (semi)global PES each require progressively more computer power. I will give a review of these types of PES separately.

3.6.1 Stretch Only Surfaces.

The stretch only PES cover the stretching co-ordinates only and so are 2 dimensional. These PES usually described in H to C distance and C to N distance. Botschwina and co-workers [131, 134, 132] have calculated a series of stretching potential and dipole functions for both HCN and HNC. The best of these HCN stretching potentials is that reported by Botschwina [132]. This potential was calculated by SCF CEPA-1 with 70 contracted Gaussian type orbitals (cGTO). 50 points were calculated. Botschwina calculated, using a variational method, only high stretching energy levels between $12\,600\text{ cm}^{-1}$ and $18\,400\text{ cm}^{-1}$. These levels deviate from experiment typically by between 80 and 100 cm^{-1} , which makes the potential quite poor at these high energies.

The best HCN stretch only dipole moment surface (DMS) was calculated with CCSD(T) and a basis of 203 cGTO’s by Botschwina *et al* [131]. HCN band intensities and transition dipole’s of strong overtones up to $23\,000\text{ cm}^{-1}$ were calculated. The results are in good agreement with experiment.

The best HNC stretch only potential and dipole surface was also reported in Botschwina *et al* [131]. Fifty potential points were calculated with CCSD(T) and using a basis of 133 cGTO’s. Energy levels calculated using the resulting potential function are in good

agreement with experiment. The HNC stretching dipole surface of Botschwina *et al* [131] was calculated with CCSD(T) and a basis of 203 cGTO's. The band intensities calculated with this dipole surface are in good agreement with the available experimental data.

The HCN and HNC band intensities calculated by Botschwina *et al* [131], prior to this work, were the best available high energy stretching intensity data. However the more powerful computers that are available today allow for the calculation of 3D potential surfaces, for triatomics, with larger basis sets than were used by Botschwina *et al* [131].

3.6.2 Partial 3D Surfaces.

Partial surfaces as their name suggests cover only part of the full molecular surface. In the case of HCN/HNC this means either the HCN minimum or the HNC minimum. In the last 20 years three *ab initio* HCN potential surfaces have been calculated and fitted. These are, in chronological order, those of Jørgensen *et al* [54], Wong and Bacskay [93] and Botschwina *et al* [133]. The best of these PES is that of Botschwina *et al* [133] who used CCSD(T) and a cc-pCVQZ basis, the biggest of the basis sets used to generate a partial PES. 123 energy points were calculated and fitted. Only relatively low lying band origins were calculated with the resulting PES. The fundamentals compare to within 5 cm^{-1} and the higher lying states compare to within 10 cm^{-1} .

Botschwina *et al* [133] also calculated and fitted a HCN dipole surface. This surface is an extension of their stretch only dipole moment surface [131] into bent nuclear configurations. 192 further dipole points were calculated with CCSD(T) and a basis of 110 cGTO's. Only the transition dipole of the ν_3 fundamental was calculated. Their calculation was in good agreement with experiment and even reproduced the unusual intensity structure of the ν_3 band for the first time, see chapter 6. However the wave-functions that were used for their calculation came from the empirical PES of Carter *et al* [136]. As a result this is not a fully *ab initio* calculation of the intensity of the ν_3 fundamental.

3.7 Global Surfaces.

The (semi-)global potential surfaces cover both the HCN and HNC minima so as a result calculations on both HCN and HNC can simultaneously be performed with them. Prior to this work 2 HCN/HNC global PES existed. The first of these PES were calculated and fitted by Bentley *et al* [94], which was later improved and republished by the same workers in Bowman *et al* [116]. The potential reported by Bowman *et al* [116] is a

spline fit to 2160 energy points calculated with CCSD(T) and an ANO type basis of roughly the same size as an aug-cc-pCVTZ basis. The core of these points were calculated on a $10 \times 10 \times 20$ grid in R, r, γ and extend to energies of $150\,000\text{ cm}^{-1}$. Vibrational HCN/HNC band origins up to $23\,000\text{ cm}^{-1}$ were calculated with a DVR technique. The calculated HCN with experiment to $5\text{-}40\text{ cm}^{-1}$ for low lying states ($E < 12000\text{ cm}^{-1}$) and $20\text{-}70\text{ cm}^{-1}$ for the high energy states. The HNC band origins reproduce experiment much less well in particular states containing an excitation of v_1 , the H to N stretch mode deviated by $40\text{-}60\text{ cm}^{-1}$ from experiment. Later Varandas and Rodrigues [173] calculated full valence complete active space (FVCAS) energies with a TZV2P basis at the unusual C-H-N geometries of the [H,C,N] system. They fitted both their new points and the CCSD(T) points of Bowman *et al* [116] with a function based on a single-valued double many body expansion (DMBE). The resulting DMBE surface fitted high energy points CCSD(T) points of Bowman *et al* [116], in the region $30\,000\text{-}50\,000\text{ cm}^{-1}$ with a marginally smaller root mean square deviation than the original surface of Bowman *et al* [116]. However the band origins calculated with the DMBE surface reproduced experiment considerably less well than the surface of Bowman *et al* [116]. The DMBE surface of Varandas and Rodrigues [173] is valid at high energies, but relatively poor at low energies. The authors themselves recommend that their surface be used for dynamical calculations such as dissociation $\text{HCN} \rightarrow \text{H} + \text{CN}$. However for the relatively low energy (less than 20000 cm^{-1}) vibration-rotation calculations that we will be performing the *ab initio* surface of Bowman *et al* [116] is better. As a result the *ab initio* Bowman *et al* [116] potential surface was the best available low energy surface prior to this work.

The *ab initio* global HCN/HNC dipole surface of Jakubetz and Lan [117] was the only surface that existed prior this work. However during the course of this work Bowman *et al* [118] published a further *ab initio* global HCN/HNC dipole surface. The dipole surface of Jakubetz and Lan [117] was fitted to over 2000 points which were calculated using the single-reference AQCC method and a TZP basis set. The single-reference AQCC method that was used for their calculations gave a poor representation near the HCN minimum when r was stretched from its equilibrium geometry. As a result this region of the DMS the surface is represented by an extrapolation from higher geometries making their DMS unreliable in this region. Jakubetz and Lan calculated some stretching band intensities with their DMS using wave functions from the PES of Bowman *et al* [116]. Their band intensities deviate significantly further from experiment than do the band

intensities calculated by Botschwina *et al* [131] from their stretch only HCN and HNC DMS.

The DMS of Bowman *et al* [118] was calculated using CCSD(T) and an aug-cc-pCVTZ basis set. 144 dipole moment points were calculated and fitted in all. However Bowman *et al* did not calculate any band intensities with their DMS. Bowman *et al* [118] used the larger of the two basis sets and the superior CCSD(T) method. As a result the Bowman *et al* [118] DMS is superior to the DMS of Jakubetz and Lan [117].

3.8 Why Use *ab initio* Surfaces?

It is clear that spectroscopically fitted potential surfaces reproduce the fitted data to levels of accuracy that are currently unachievable by *ab initio* means alone. For example the *ab initio* surface of Bowman *et al* [116] reproduces the HCN fundamentals to between 3 and 20 cm^{-1} , but the empirically corrected surface of Wu *et al* [119] reproduces the fundamentals to less than 0.01 cm^{-1} . So why use *ab initio* surfaces? The weakness of spectroscopically fitted surfaces lies in the calculation of data that is outside region in which experimental data is available. For example Wu *et al* [119] fitted data with bend excitations up to $v_2 = 5$ to within 0.01 cm^{-1} . Recently experimental data [147] up to $v_2 = 9, 10$ has become available. This new data is reproduced much less favorably to within 10 cm^{-1} , only marginally better than *ab initio* surface of Bowman *et al* [116]. A further example is shown in figure 3.8. This figure shows the obs-calc error for water for the *ab initio* calculations of Polyansky *et al* [95] and the calculations of Partridge and Schwenke [96]. Polyansky *et al* [95] used an *ab initio* surface whereas Partridge and Schwenke [96] used an empirical potential. The results of Partridge and Schwenke [96] have a smaller error than the *ab initio* results of Polyansky *et al* [95]. However the error on the calculations of Partridge and Schwenke [96] increases with J especially for the high (051)-(040) transition. In contrast the error on the *ab initio* calculations remains relatively constant. This highlights that spectroscopically fitted PES reproduced new experimental data to an unpredictable accuracy and often considerably are worse than *ab initio* PES. The linelist calculation undertaken in this thesis probes many regions of the spectrum where no experimental data is available. As a result an *ab initio* PES will be used to avoid any potential problems in these 'uncharted' regions of the spectrum that may occur when using spectroscopically fitted PES.

The global PES of Bowman *et al* [116] and the DMS of Jakubetz and Lan [117] use

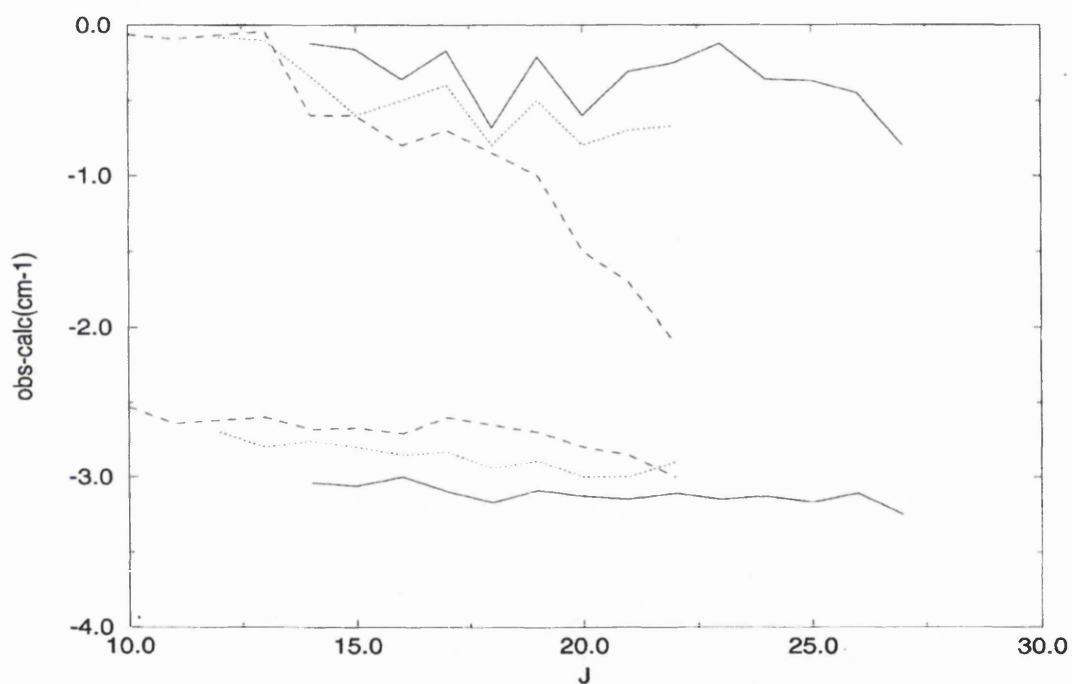


Figure 3.3: A comparison of typical band errors (Obs-Cal) for water for the *ab initio* linelist of Polyansky *et al* [95] (lower lines) and the linelist of Partridge and Schwenke [96] (upper lines). The solid lines are (031)-(020), dotted line (041)-(030) and dashed lines (051)-(040). Figure taken from ref. [95].

basis sets that are relatively small by todays standards. As a result new global *ab initio* PES and DMS were fitted as part of this work. The new PES and DMS are discussed in chapter 4 and were published as part of the work of van Mourik *et al* [23].

Chapter 4

New *ab initio* Semi-Global HCN/HNC Surfaces.

An extensive semi-global *ab initio* PES has been calculated and fitted by Bowman *et al* [116] and an *ab initio* semi-global dipole surface has been calculated by Jakubetz and Lan [117]. Both these surfaces have been calculated with basis sets that are by today's standards small. It was therefore decided that new semiglobal *ab initio* PES and dipole surfaces would be developed for this work. The PES of Bowman *et al* and the dipole surface of Jakubetz and Lan have been reviewed fully in section 3.6.

In this chapter, I present fits to semiglobal dipole moment surfaces of the [H,C,N] system and a number of *ab initio* potential energy surfaces PES. These surfaces were fitted to results of electronic structure calculations external to this work. Electronic structure calculations were performed by van Mourik, with a number of different basis sets. Also used in the potential surface fits are the electronic calculations of Bowman *et al* [116]. In addition to these calculations a consideration of electronic relativistic effects and a simple adiabatic correction to the Born–Oppenheimer approximation, has been performed by my collaborator A. Császár. I also present a relativistic and adiabatic surface fitted to the calculations of Császár. The calculations of van Mourik and Császár along with the fitted surfaces are published in van Mourik *et al* [23].

4.1 Electronic Calculations.

Although the electronic calculations were not performed explicitly as part of this thesis, the accuracy of a surface is limited by the method of calculation of, and number of electronic

points used. It is therefore necessary to give a brief discussion of these calculations.

The computations of Bowman *et al* [116], performed at the CCSD(T) level with an $[4s3p2d1f/4s2p1d]$ atomic natural orbital (ANO) type basis, employed a very extended grid comprising 2160 points. The accuracy of the PES of Bowman *et al* is limited by the accuracy of the ANO basis, which is not as large as the basis sets employed in similar studies today. It was therefore one of the aims of this thesis to improve the PES of Bowman *et al* by including electronic structure calculations performed with a higher level basis set.

As it is not practical to re-compute CCSD(T) energies at such an extensive grid as that of Bowman *et al* with a large basis set, a grid of points with co-ordinates in the same range as used by Bowman *et al* was selected. This grid of points was then truncated so that only points which lay less than $25\,000\text{ cm}^{-1}$ above the absolute minimum of the Bowman *et al* surface remained. However this selection still resulted in too many points, so only those grid points were retained for which the H – CN Jacobi angle, θ , was equal to 0, 20, 40, 60, 80, 100, 120, 140, 160, or 180° ; *i.e.*, only half of the angular grid was retained. This procedure resulted in a total of 243 points on a $10\times10\times10$ grid, in which the R and r co-ordinates were equally spaced over the ranges:

$$1.5 \leq R(a_0) \leq 4.5$$

$$1.8 \leq r(a_0) \leq 2.8$$

Finally, a variety of high-accuracy *ab initio* methods were used to determine the relative energy and geometry of three stationary points of the ground-state [H,C,N] system: the two minima (HCN and HNC) and the saddle point (transition state) connecting them.

Electronic energies and dipole moments were calculated at the selected 243 grid points employing cc-pCVQZ CCSD(T) wave functions and correlating all electrons. At each grid point the dipole moment was computed via the finite-field method.

To check that the coarseness of the grid was not to blame for problems at the HNC minimum (see below), 14 additional energy calculations were run, at the same level of theory, at new grid points about the HNC minimum; these points were not used in the final fit. 17 calculations were repeated with the larger aug-cc-pCVQZ basis also about the HNC minimum. This was done to improve the surface around the HNC minimum (see below).

The co-ordinates and energies of the 3 stationary points were optimised with the yet larger cc-pCV5Z basis. These points were used to re-position the minima and saddle points

of the PES.

4.1.1 Auxiliary Correction Calculations

It has been found that electronic relativistic effects and the adiabatic or Born–Oppenheimer Diagonal Correction (BODC) can have a small but significant effect on the effective potential surface, and hence, on the calculated vibration-rotation levels of small molecules [104, 105, 100]. Therefore, they have been considered as part of this study. Electronic relativistic corrections were obtained using all-electron aug-cc-pCVDZ CCSD(T) wave functions and the DPT approach of Kutzelnigg [97, 98]. BODC energy points were computed at the TZ2P RHF level. All these calculations were performed for 243 geometries representing our initial grid.

4.2 Potential Energy Surfaces

In this work it was decided that the potential surface would be generated by a least squares fit rather than by using a bicubic spline for several reasons (see section 2.10). Firstly least squares fitting (LSF) provides us with a standard deviation of the point from the fitted function, giving an idea as to how good the overall fit is. Secondly the 2 sets of points that we aim to fit separately, define surfaces that differ slightly in both steepness and depth of the potential (see below), a spline would pass directly through both sets of points creating a surface that has a 'wobble' in its fine structure (400cm^{-1} in our case). Least squares fitting adapts a chosen function to the given set of points, so if a suitable number of degrees of freedom are chosen in the fitting function the LSF surface will be smoother than the spline. When using LSF, a fitting function is chosen that is believed to resemble the true form of the surface. In contrast spline interpolation assumes no knowledge of the shape of the surface and as a consequence requires many more points to achieve a surface as good as that generated by an LSF. Finally an LSF allows us to weight our 2 sets of points differently, giving them a weaker or stronger effect on the fit depending on, in this case, the level of theory used to calculate the points.

The function used to represent the HCN potential in this thesis was chosen to be

$$V(R, r, \gamma) = \sum_{i,j,k} A_{ijk} X^i(R, r, \gamma) Y^j(r, \gamma) P_k(\cos \gamma) \quad (4.1)$$

where (R, r, γ) are Jacobi co-ordinates with linear HCN at $\gamma = 0$. A_{ijk} is a constant for a particular i , j and k , and P_k are Legendre polynomials for the angular (γ) component

of the fit. X and Y are functions, primarily, of the R and r co-ordinates respectively, that are based on Morse co-ordinates transformations, which have been previously used as fitting functions for HCN stretching co-ordinates by Wong *et al* [93], where

$$X(R, r, \gamma) = [1 - e^{-\alpha_R(\gamma)[R - R_e(\gamma, r)]}] \quad (4.2)$$

$$Y(r, \gamma) = [1 - e^{-\alpha_r[r - r_e(\gamma)]}] \quad (4.3)$$

So X^2 and Y^2 are simply Morse potentials, with R_e and r_e the co-ordinates of the minimum and with α_R and α_r governing the steepness of the potential. Over the HCN/HNC system the parameters R_e , r_e , α_R and α_r show dependences on angular position of the H nucleus, these angular dependence are taken into account in the functional forms of R_e , r_e , α_R and α_r :

$$R_e(\gamma, r) = A_{R_e} + B_{R_e} \cos \gamma + C_{R_e} \cos^2 \gamma + D_{R_e} r^2 \cos^2 \gamma \quad (4.4)$$

$$r_e(\gamma) = A_{r_e} + B_{r_e} \cos \gamma + C_{r_e} \cos^2 \gamma \quad (4.5)$$

$$\alpha_R(\gamma) = A_{R_\alpha} + B_{R_\alpha} \cos \gamma + C_{R_\alpha} \cos^2 \gamma \quad (4.6)$$

with α_r a constant.

The angular dependences of R_e and r_e of the VQZANO+ potential surface is shown in figure 4.1, R_e also shows a less strong but significant dependence on r . The experimental H-C stretch fundamental of HCN differs by over 10% from its H-N stretch HNC fundamental counterpart, whereas the C-N stretch fundamental of HCN and its HNC counterpart differ by only 3.6% (see tables 5.9 and 5.10). This suggests a strong angular dependence of α_R , confirmed in figure 4.2 and a less strong angular dependence of α_r .

Using these functional forms for R_e , r_e and α_r with initially $R_e(\gamma, r)$ and $r_e(\gamma)$ as fits to the least energy isomerisation (LEI) path and α_r as a constant, reduced the standard deviation by a factor of 3. However if we allowed the parameters of these functions to change via a simple non-linear fitting method (see section 2.10.2) we were able to achieve a yet lower standard deviation of the overall potential energy surface. This functional form yielded a fit to the initial 243 *ab initio* potential points calculated in this work with a standard deviation of less than 3 cm^{-1} and an RMS deviation of less than 1.5 cm^{-1} . There are 180 terms in this fit with $i_{max} = 4$, $j_{max} = 5$ and $k_{max} = 5$. This fit shall be hereafter referred to as the VCVQZ potential surface.

The HCN and HNC minima and the LEI path of the VCVQZ surface occur at significantly different geometries and energies than those of the surface of Bowman *et al* [116], see table 4.1 and figures 4.3 and 4.4. This results in a large standard deviations (> 800

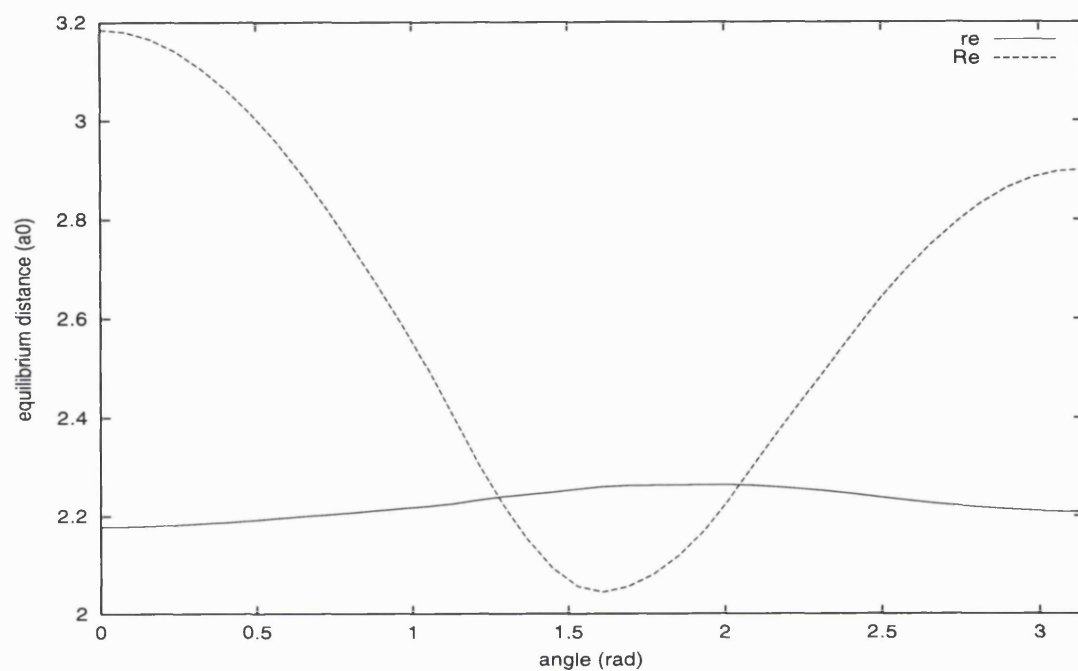


Figure 4.1: Plot of the equilibrium distances R_e and r_e along the LEI path as a function of the angle γ .

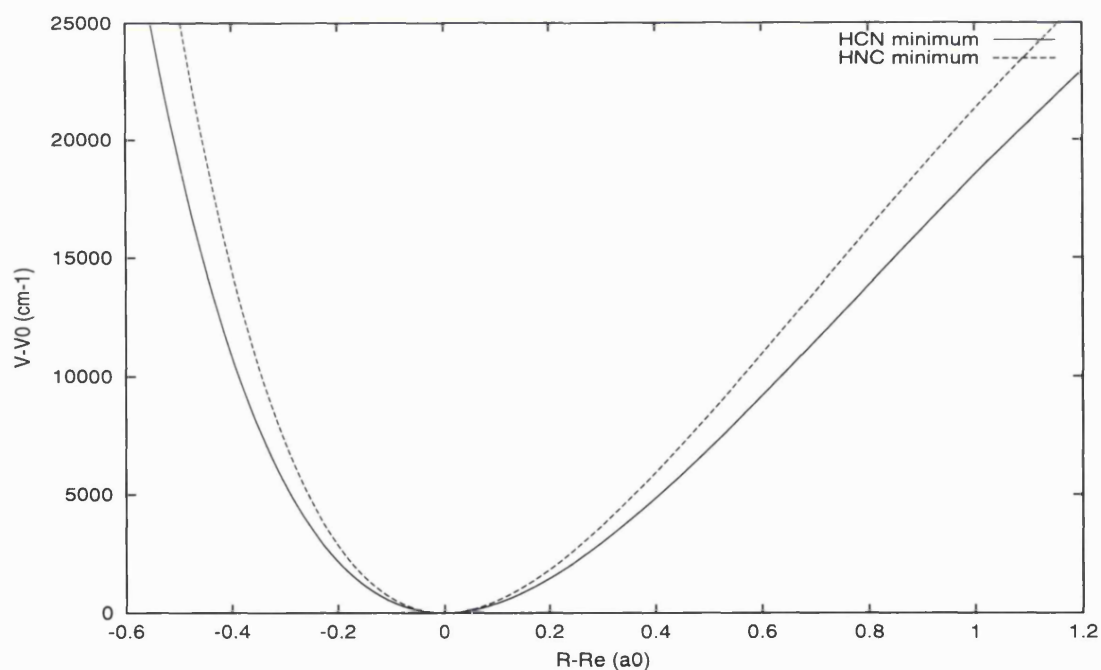


Figure 4.2: HCN and HNC minimum in the R co-ordinate, with r fixed to local value of r_e and the potential set to zero at the local minimum ($V - V_0$). $R - R_e$ is displacement of R from local R minimum. Plot clearly shows differences in the steepness of the potential at the 2 geometries.

cm^{-1}) when both these grids of points are simultaneously fitted. The differences between the VCVQZ surface and the surface of Bowman *et al* are a result of the different electronic basis sets used for the calculation of each surface.

This problem was solved in part by 'shifting' the potential points of Bowman *et al* in the r and R co-ordinates, and in energy as a function of angle γ . So that a potential surface fitted to the shifted Bowman *et al* points would have the same co-ordinates and energy along the LEI path and at the 2 minima as the VCVQZ surface. Initially we truncated the points of Bowman *et al* at 25000 cm^{-1} , leaving 508 points, and then least squares fitted them with our fitting function equation 4.1. Using 216 terms and $i_{max} = 5$, $j_{max} = 5$ and $k_{max} = 5$, we achieved a standard deviation of 3 cm^{-1} , an RMS deviation of 2.3 cm^{-1} and an absolute deviation of 1.7 cm^{-1} . This fit will be hereafter referred to as the VANO25 surface.

The energy and r and R co-ordinates of the LEI path of the VANO25 surface and those of the VCVQZ surface were calculated at 40 equally spaced values over the range $0 \leq \gamma \leq \pi$. This allowed the determination of differences in co-ordinates and energy of the LEI paths of the 2 surfaces, at these 40 angles. Legendre polynomials up to fifth order were used to least squares fit the differences in the co-ordinates and energy along the LEI path of the 2 surfaces at the 40 angles. This gives a function with which we can 'shift' the points of Bowman *et al* at any value of the angle γ . The 'shifted' Bowman *et al* points truncated at 25000 cm^{-1} were least squares fitted. This surface is here after referred to as the VANO25S surface.

Figure 4.5 shows that although the minima and LEI of the VCVQZ surface and the VANO25S surface coincide in the R and r co-ordinates and in energy, the steepness of the slope of the potential in the R and r co-ordinates of the VANO25S surface is less than that of the VCVQZ surface. This results in a large difference in energy (200 cm^{-1}) between the 2 surfaces at high displacements from the local minimum. This, again, will quite clearly cause problems when simultaneously fitting the 243 cc-pCVQZ points and the 'shifted' points of Bowman *et al*.

A weighting system was chosen to overcome this problem. The greatest weight of 5000 was given to the 243 cc-pCVQZ points, to reflect their greater level of theory and reliability. A functional form was chosen for the weighting of the Bowman *et al* points. This function gives a lower weighting to those points which deviate significantly in energy from the cc-pCVQZ points. This deviation is a result of the difference in steepness of

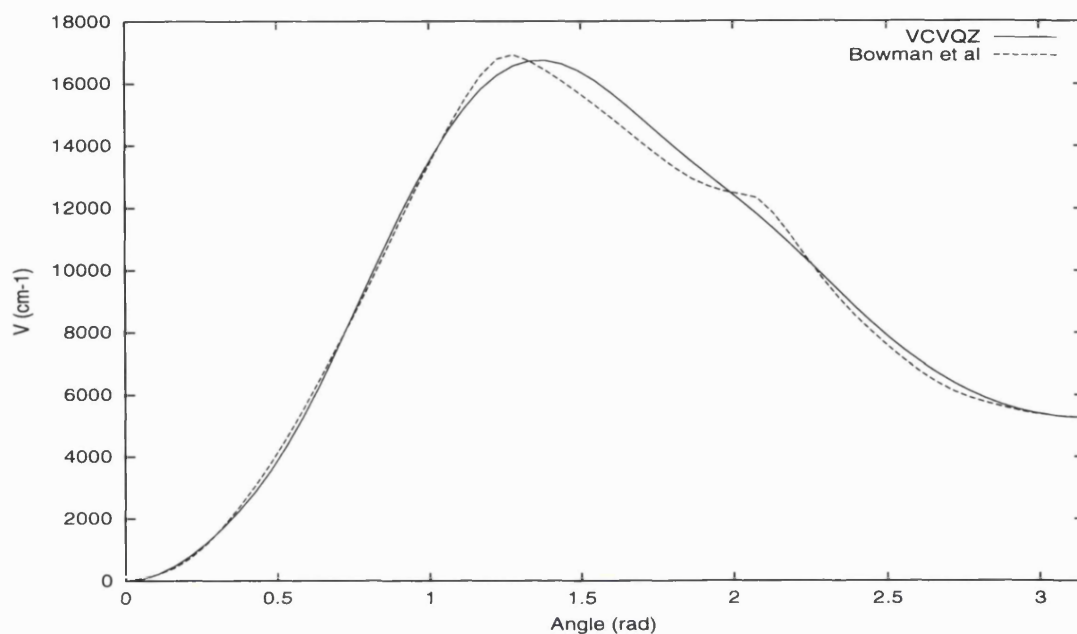


Figure 4.3: The potential energy along the least energy isomerisation path of the surface of Bowman *et al* [116] and the VCVQZ surface. This clearly illustrates that the cc-pCVQZ points calculated for this work and the points calculated by Bowman *et al* differ significantly in energy, particularly at the HNC side of the potential.

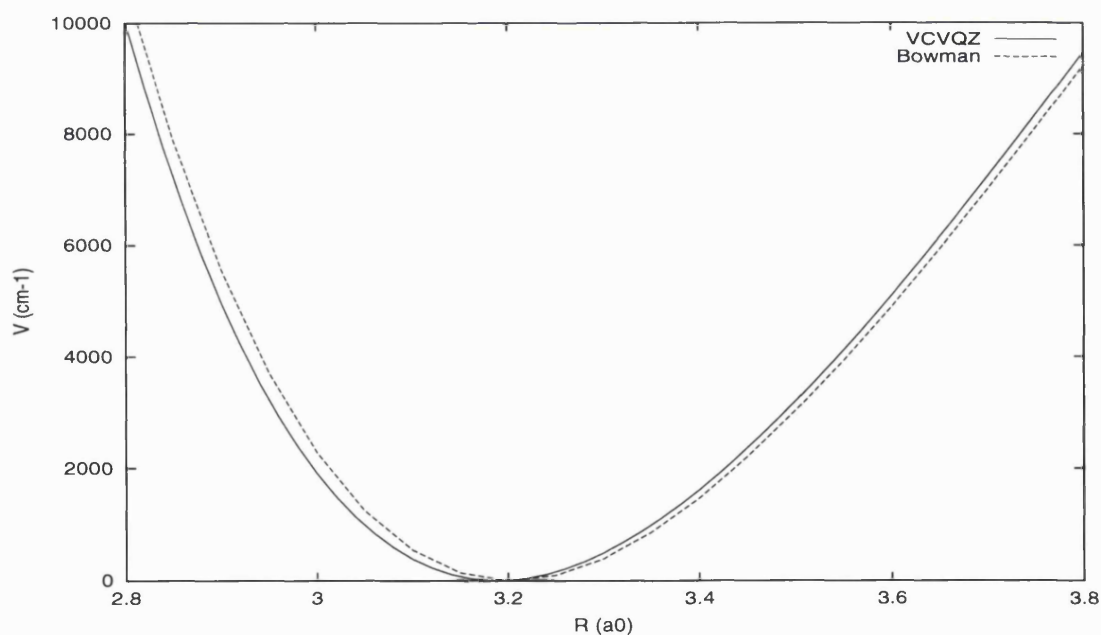


Figure 4.4: A cut through the HCN minimum in the R co-ordinate of the VCVQZ surface and the surface of Bowman *et al* [116]. This clearly illustrates that the position of the minimum in the R co-ordinate occurs at different distances in each surface, resulting in a significant difference in energy between the surfaces at a given co-ordinate.

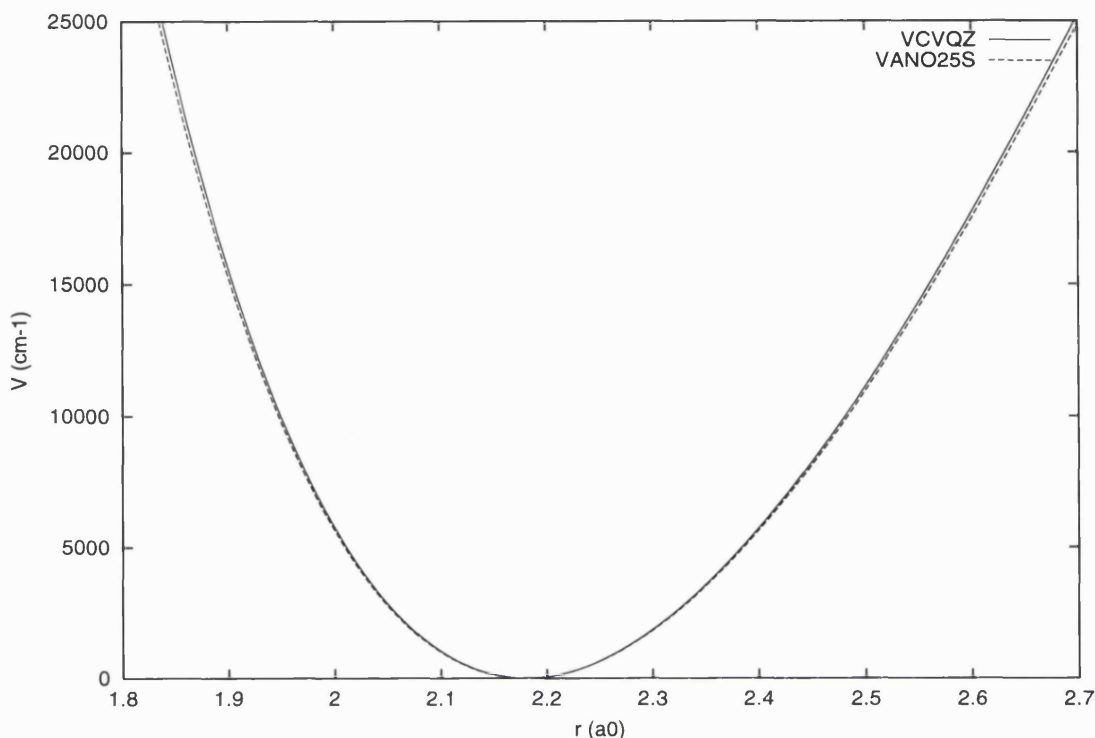


Figure 4.5: A cut through the HCN minimum in the r co-ordinate of the VCVQZ and VANO25S surfaces. This clearly illustrates that although the position of the minimum in the r co-ordinate of each surface are now coincident, the steepness of the VANO25s surface is less than that of the VCVQZ surface.

the slope of the potential in the r co-ordinate of the two sets of points. The functional form of the 'shifted' Bowman *et al* points weighting was based on the inverse square of the displacement of r from the $r_e(\gamma)$ on the LEI path:

$$W = \frac{w(V)}{1 + (200(r - r_e(\gamma))^2)} \quad (4.7)$$

where W is the weight given to the point and $w(V)$ is a further energy dependent weighting factor, given by:

$$\begin{aligned} V < 25000\text{cm}^{-1}, w(V) &= 100 \\ 25000\text{cm}^{-1} \leq V < 35000\text{cm}^{-1}, w(V) &= 10 \\ V \geq 35000\text{cm}^{-1}, w(V) &= 0.5 \end{aligned}$$

The weighting factor, ω , is designed to reflect the greater importance of the accuracy of this fit at the low energy regions ($< 25000\text{cm}^{-1}$). The 'shifted' Bowman *et al* points were truncated at 45700cm^{-1} , dissociation energy of HCN [106], so that the very high energy

points of Bowman *et al* did not interfere with the fit at low energies. By weighting the points in this way, we fitted both the potential points calculated in this work and the remaining 1527 'shifted' points of Bowman *et al*, with 252 terms i_{max} and j_{max} of 5 and a k_{max} of 6 were used. The fit, hereafter referred to as the VQZANO1 surface, had an RMS deviation of 3.3 cm^{-1} from the points calculated in this work, an over all standard deviation of 412 cm^{-1} , an absolute deviation of 211 cm^{-1} and an RMS deviation of 376 cm^{-1} . This surface fits the cc-pCVQZ points to a good degree of accuracy, as well as adhering to the high energy ($>25000 \text{ cm}^{-1}$) shifted Bowman *et al* points, so maintaining a realistic shape of potential at high energies.

4.2.1 Morphing the Potential Surface

The vibrational fundamental band origins of both HCN and HNC, calculated with the VQZANO1 potential surface deviate by 4 cm^{-1} or less from the observed band origins except for the HN stretching fundamental (ν_1) of HNC (see tables 5.9, 5.10). This fundamental deviates from the observed value by 20 cm^{-1} , an anomalously large deviation.

An attempt was made to include extra points in our fit, calculated at the CCSD(T)/cc-pCVQZ level in the region of HNC minimum (see section 4.1). This made little difference to the HNC band origins suggesting that this was not a problem with the coarseness of our grid. However we found the cc-pCVQZ basis used to calculate our points is too small to model the HNC part of the potential accurately. With limited computer time 17 new *ab initio* points at the aug-cc-pCVQZ CCSD(T) were calculated (see section 4.1).

We then adapted our initial potential by 'morphing' it [108, 109] using the function

$$V_{morph}(R, r, \gamma) = V_{orig}(R + \rho(R, \gamma), r, \gamma). \quad (4.8)$$

Here V_{morph} is the morphed surface, V_{orig} is the original surface and $\rho(R, \gamma)$ is a distance scaling function:

$$\rho(R, \gamma) = \alpha(\gamma) \sum_i \sum_j B_{ij} (R - R_{LEI}(\gamma))^i \cos^j \gamma \quad (4.9)$$

Where B_{ij} are the coefficients of the fit and $R_{LEI}(\gamma)$ is the local R co-ordinate of the LEI path and $\alpha(\gamma)$ is a damping function with the conditions

$$\alpha(\gamma) \rightarrow 0 \text{ when } \gamma \rightarrow 0$$

$$\alpha(\gamma) \rightarrow 1 \text{ when } \gamma \rightarrow \pi$$

These conditions force $\rho(R, \gamma)$ to be zero at the low angles that correspond to the HCN

side of the surface. This is the part of the surface which we do not wish to be changed by this morphing. The functional form for $\alpha(\gamma)$ is given by

$$\alpha(\gamma) = \exp(-(0.6(\gamma - \pi))^6) \quad (4.10)$$

We used the equation 4.8 with 9 terms and $i_{max} = 2$ and $j_{max} = 2$, to morph the VQZANO1 surface with the 17 new more accurate points. The morphed surface has a standard deviation of 4 cm^{-1} from the 17 aug-cc-pCVQZ points. The HN stretching fundamental of HNC calculated from the morphed surface improved to within 14 cm^{-1} of the experimental value. The other vibrational fundamentals calculated from the morphed surface are almost unchanged from those calculated with the VQZANO1 surface as intended. This problem at the HNC end suggests that HNC has a more complex and diffuse electronic structure than HCN. Consequently this is why the larger aug-cc-pCVQZ basis set was needed to improve the accuracy of the potential surface at HNC geometries.

4.2.2 Critical Point Mappings.

Finally, we adjusted the potential so that the minima and saddle point were coincident in energy and co-ordinates with the 3 cc-pCV5Z points calculated at the critical points (see section 4.1). Co-Ordinate mappings for R, r and γ and an energy scaling function were least squares fitted to the 3 cc-pCV5Z points with the co-ordinates and energy of the minima and saddle point of the morphed VQZANO1 surface. The functional forms for these mappings and energy scaling function are as follows.

$$r_{map} = r_{orig} + A_r + B_r f^4(\gamma) \quad (4.11)$$

$$R_{map} = R_{orig} + A_R + B_R f^4(\gamma) \quad (4.12)$$

$$\gamma_{map} = \gamma_{orig} + B_\gamma f^{16}(\gamma) \quad (4.13)$$

$$V_{scale} = V_{orig} + A_V g(\gamma) + B_V f^{16}(\gamma) \quad (4.14)$$

In these equations A and B are the coefficients of the mapping fit and $f(\gamma)$ and $g(\gamma)$ are functions of the angle γ . The R and r co-ordinates of the 3 cc-pCV5Z points and the R and r co-ordinates of the minima and saddle point in the morphed VQZANO1 potential deviate by the greatest amount at the saddle point ($\gamma = 1.3347$), while the deviations in R and r at the HCN minimum are roughly the same as those at the HNC minimum. Taking these factors into account a function for $f(\gamma)$ that would peak at $\gamma = 1.3347$ whilst $f(\gamma) = 0$ when $\gamma = 0$ and $\gamma = \pi$ was chosen to be:

$$f(\gamma) = \sin \gamma + [0.131325 \sin(2\gamma)] \quad (4.15)$$

The 4th power of $f(\gamma)$ in equations 4.11 and 4.12 was chosen to 'sharpen' the peak so that the mapping at the saddle point would not influence the HCN and HNC minima regions. Using a power of $f(\gamma)$ lower than 16 in equations 4.13 and 4.14 was found to cause problems with the bending vibrational band origins calculated from the morphed surface with co-ordinate mappings. For the energy scaling the damping function equation 4.15 was used, with a $g(\gamma)$ function, where $g(\gamma) = 0$ for HCN geometries. The $g(\gamma)$ function used in this work is

$$g(\gamma) = \tan^{-1}[15(\gamma - 1.2)] + \pi/2 \quad (4.16)$$

The above functions were used to map and energy scale the morphed VQZANO1 surface to the 3 cc-pCV5Z. The mapped and morphed VQZANO1 surface will be referred to as the VQZANO2 surface hereafter.

4.3 The Relativistic and DBOC Correction Surfaces

The electronic relativistic correction and Diagonal Born-Oppenheimer correction (DBOC) points were both least squares fitted with the function

$$C(R, r, \gamma) = \sum_i \sum_j \sum_k A_{ijk} R^i r^j P_k^0(\cos \gamma). \quad (4.17)$$

These surfaces proved to be far smoother than the potential energy surface, so only 80 coefficients with $i_{max} = 3$, $j_{max} = 3$ and $k_{max} = 4$ were required to fit to the relativistic correction points with a standard deviation of 0.3 cm^{-1} . The relativistic correction is $+5.86 \text{ cm}^{-1}$ at the HCN minimum, $+17.27 \text{ cm}^{-1}$ at the HNC minimum and -16.77 cm^{-1} at the saddle point. For the DBOC surface we used $i_{max} = 2$, $j_{max} = 3$ and $k_{max} = 4$, which yielded a standard deviation of 0.93 cm^{-1} . For the HCN isotopomer, the DBOC is -1.65 cm^{-1} at the HCN minimum, -7.64 cm^{-1} at the HNC minimum, and 6.37 cm^{-1} at the saddle point. Figures 4.6, 4.8 and 4.10 show contour plots of our VQZANO2 potential surface with relativistic and DBOC corrections (referred to as VQZANO+ surface). To aid the eye, figures 4.7 and 4.9 show 3D plots with colour contours of the VQZANO+ surface.

Table 4.1 shows the geometries of the critical points of our surfaces, those of the surface of Bowman *et al* [116] and some experimentally determined equilibrium geometries.

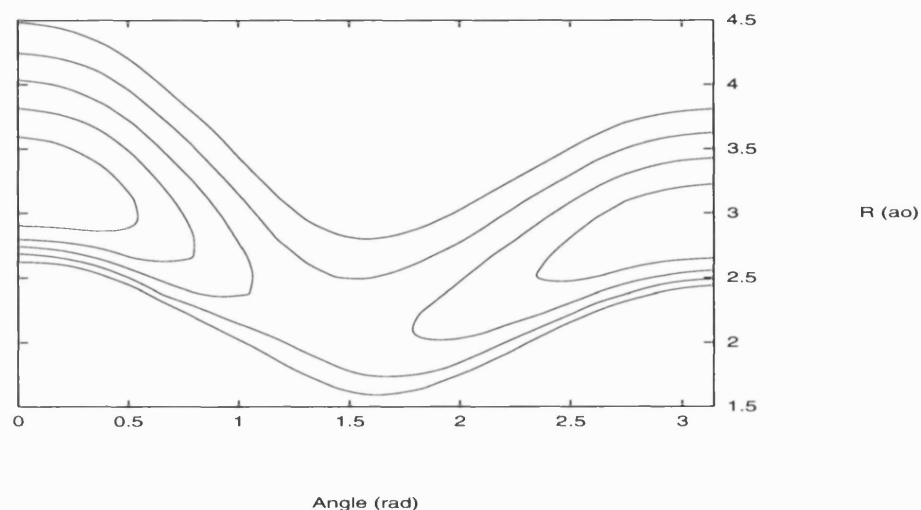


Figure 4.6: Contour plot of HCN/HNC VQZANO+ surface in R and γ co-ordinates with r fixed to the near HCN ($\gamma = 0$) equilibrium value of $2.179 a_0$. The contours have a minimum value of 5000 cm^{-1} and a maximum value of 25000 cm^{-1} , relative to the HCN minimum, with increments of 5000 cm^{-1} .

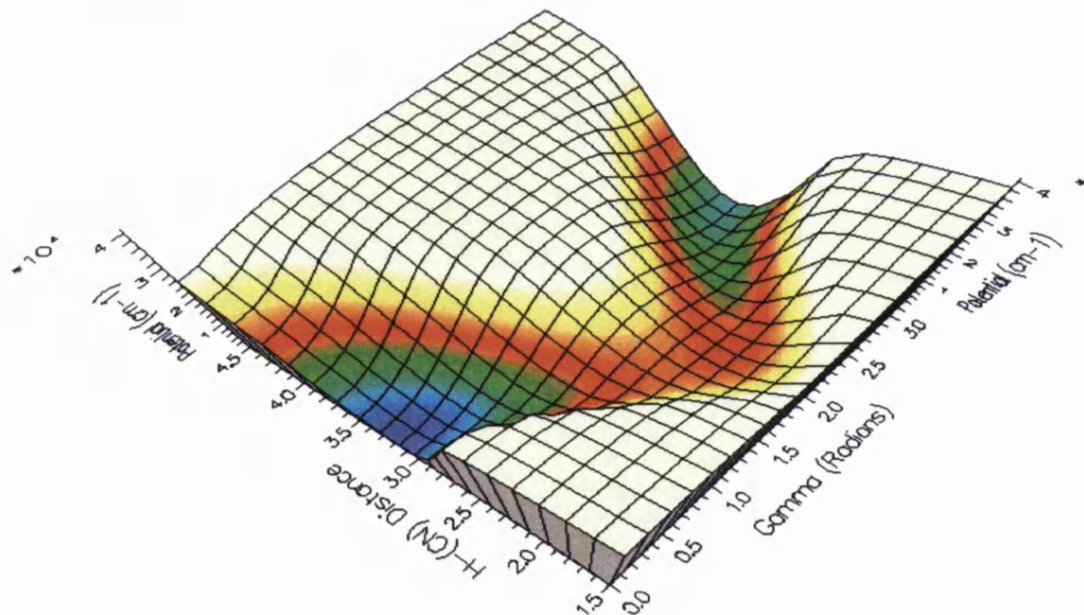


Figure 4.7: 3D plot with colour contours of the HCN/HNC VQZANO+ surface in R and γ co-ordinates with r fixed to the near HCN ($\gamma = 0$) equilibrium value of $2.179 a_0$, all distances are in a_0 . At energies above $25\,000 \text{ cm}^{-1}$ the plot is artificially leveled to show the low energy regions in detail.

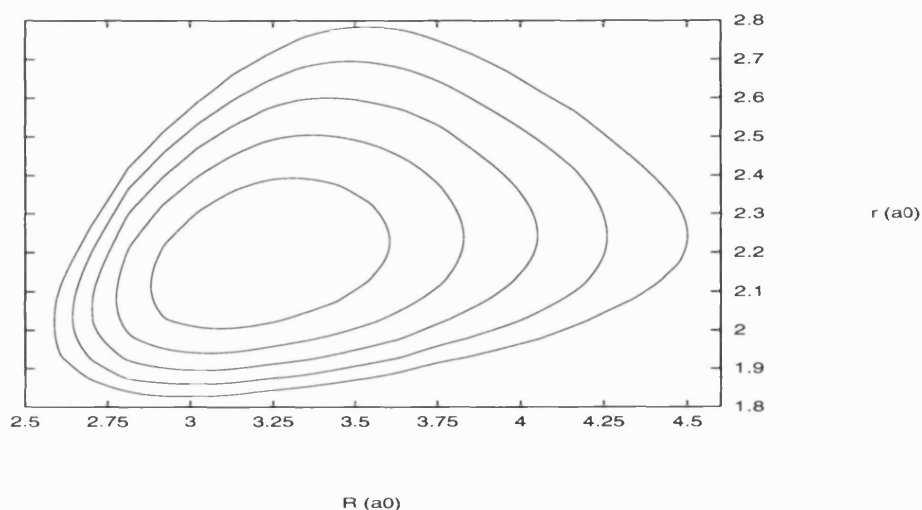


Figure 4.8: HCN minimum of VQZANO+ surface in R and r co-ordinates with γ fixed to the HCN equilibrium value of 0 radians. The contours have a minimum value of 5000 cm^{-1} and a maximum value of 25000 cm^{-1} , relative to the HCN minimum, with increments of 5000 cm^{-1} .

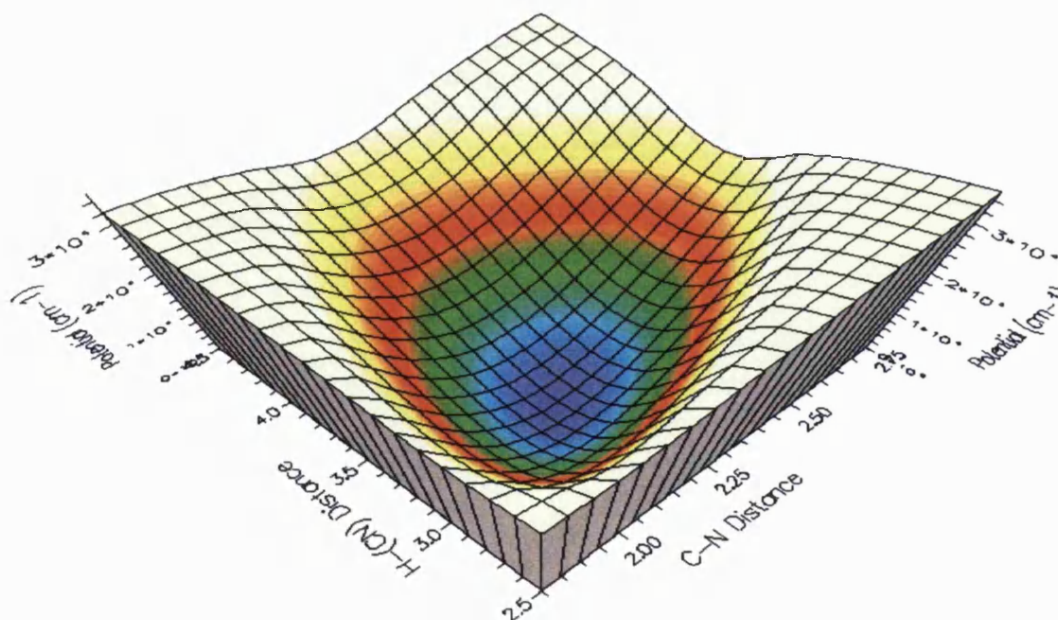


Figure 4.9: 3D plot with colour contours of the HCN minimum of VQZANO+ surface in R and r co-ordinates with γ fixed to the HCN equilibrium value of 0 radians, distances are in a_0 . At energies above $25\,000 \text{ cm}^{-1}$ the plot is artificially leveled to show the low energy regions in detail.

For the HCN minimum our VQZANO+ surface agrees to 4 significant figures with the experimentally determined equilibrium bond lengths, where as the critical points of the Bowman *et al* surface agree only to 3 figures and is worse for the C to N distance than the R co-ordinate. There is a similar pattern for the HNC case, in which the critical points of the surface of Bowman *et al* agree much less well with experiment than do the critical points of the VQZANO+ surface. The likely cause of this less desirable position of the critical point of the surface of Bowman *et al* is due to the smaller basis set employed by Bowman *et al*. This is also echoed by the large difference between experimental and calculated band origins of the Bowman *et al* surface (50cm⁻¹ for HNC C to H stretch) compared with the VQZANO+ surface, see tables 5.9 and 5.10 and section 5.4.

Table 4.2 gives a summary of the potential surfaces presented here.

4.4 The Dipole Surface Fit

4.4.1 Fit to Jakubetz and Lan Dipole Points.

The 2055 SCF/AQCC dipole points calculated by Jakubetz and Lan [117] were provided by Jakubetz [115]. These points were then least squares fitted with the same function as used by Jakubetz and Lan.

$$\mu_z(R, r, \gamma) = \sum_{i=0}^4 \sum_{j=0}^4 \sum_{k=0}^{10} A_{ijk} R^i r^j P_k^0(\cos \gamma) \quad (4.18)$$

$$\mu_x(R, r, \gamma) = \sum_{i=0}^4 \sum_{j=0}^4 \sum_{k=1}^{10} A_{ijk} R^i r^j P_k^1(\cos \gamma) \quad (4.19)$$

This this yielded fits with standard deviation of 0.0104 au for the z component and 0.00353 au for the x component.

Jakubetz and Lan experienced problems with their electronic structure calculations at small to large displacements from the C-N equilibrium near the HCN minimum. This was caused by the inapplicability of the single reference SCF method in this region. Consequently they left out their dipole points in this region and for used an extrapolation from higher angles in their surface. This was not performed in this fit to the dipole points of Jakubetz and Lan.

Calculations with this surface are given in tables 5.13 and 5.14. The calculations with this surface show significant deviation from experiment in the HCN C to N stretch mode.

This problem is a reflection of the poor representation of the HCN C to N co-ordinate of the single reference SCF method.

There is also a great sensitivity to the use of different wavefunctions for the HCN C to N fundamental. This is likely to be caused by the unusual intensity structure of this band, see chapter 6.

4.4.2 Fit to CCSD(T) Dipole Points.

The x and z components CCSD(T) dipole points (see section 4.1) were least squares fitted using functions similar to those used by Brocks *et al* [110] to represent the dipoles of KCN and LiCN:

$$\mu_z(R, r, \gamma) = \sum_i \sum_j \sum_{k=0}^{k_{max}} A_{ijk} \exp(B_i R) \exp(C_j r) P_k^0(\cos \gamma) \quad (4.20)$$

$$\mu_x(R, r, \gamma) = \sum_i \sum_j \sum_{k=1}^{k_{max}} A_{ijk} \exp(B_i R) \exp(C_j r) P_k^1(\cos \gamma) \quad (4.21)$$

The z axis of our dipole surface lies along the CN bond and the x axis lies perpendicular to the x axis so that the H nucleus bends in xz plane. The dipole surfaces are far smoother than the potential surface, so for μ_z , we used $i_{max} = 2$, $j_{max} = 2$ and $k_{max} = 6$ and achieved a standard deviation of 0.008 D and an absolute deviation of 0.005 D. For μ_x , we used $i_{max} = 2$, $j_{max} = 2$ and $k_{max} = 5$ and achieved a standard deviation of 0.002 D and an absolute deviation of 0.001 D. The dipole points of this work are limited to nuclear geometries that correspond to energies of less than 25000 cm^{-1} , consequently the dipole surfaces can only be considered reliable for energies below this value. Figures 4.11 and 4.12 show contour plots of the dipole surface in the R and γ co-ordinates. A problem with the z component of the dipole surface is evident at intermediate angles and larger R , this corresponds to high energy regions of the PES for which no dipole points were available for the fit. This dipole surface will be referred to as the μ_{QZ} DMS.

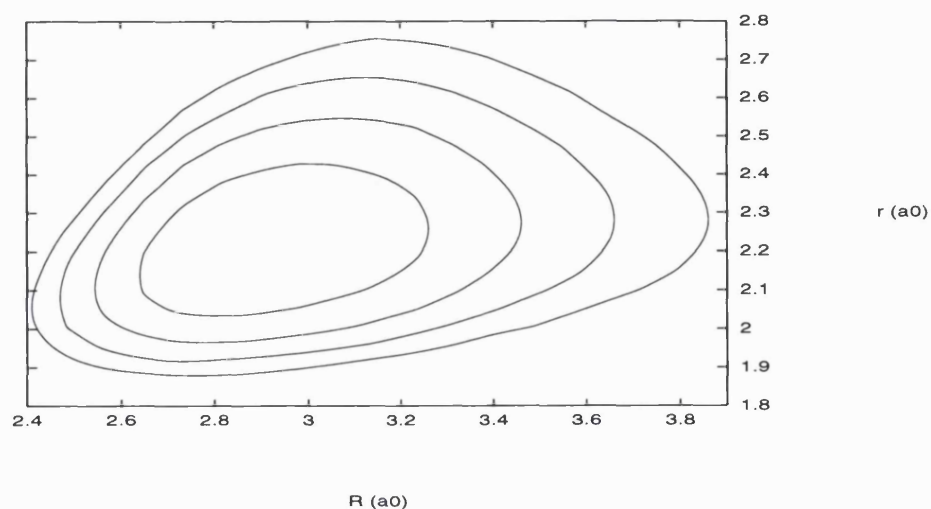


Figure 4.10: HNC minimum of VQZANO+ surface in R and r co-ordinates with γ fixed to the HNC equilibrium value of π radians. The contours have a minimum value of 10000 cm^{-1} and a maximum value of 25000 cm^{-1} , relative to the HCN minimum, with increments of 5000 cm^{-1} .

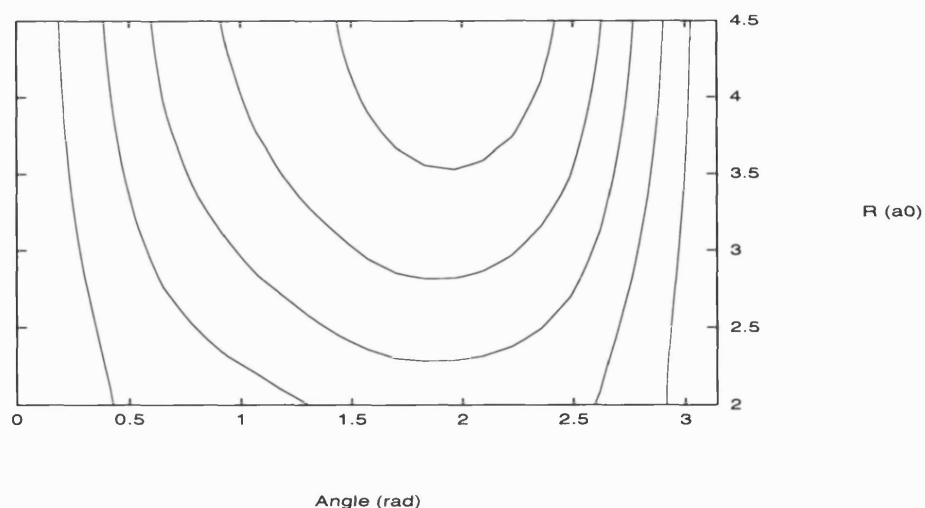


Figure 4.11: Contour plot of HCN/HNC x component of dipole surface in R and γ co-ordinates with r fixed to the near HCN equilibrium value of $2.179 a_0$. The contours have a minimum value of $0.2 a_0$ and a maximum value of $1 a_0$, with increments of $0.2 a_0$. The x dipole component is zero at $\gamma = 0$ and $\gamma = \pi$.

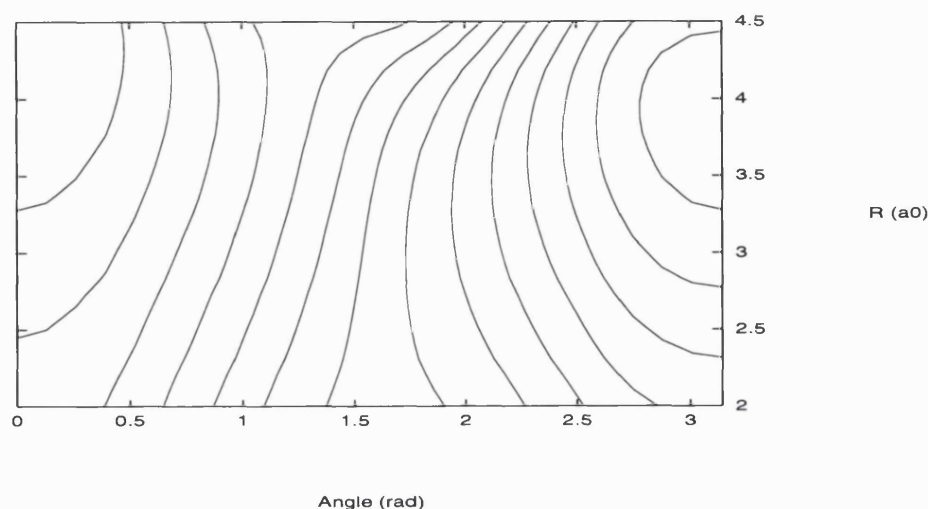


Figure 4.12: Contour plot of HCN/HNC z component of dipole surface in R and γ co-ordinates with r fixed to the near HCN equilibrium value of $2.179 a_0$. The contours have a minimum value of $-1.2 a_0$ on the HCN side and a maximum value of $1.4 a_0$ on the HNC side, with increments of $0.2 a_0$.

Table 4.1: The bond distances (R and r in a_0) and the relative energy (V in cm^{-1}) of the minima and saddle points of various *ab initio* potential energy surfaces and sets of potential points. Energy of the HCN minimum is set to zero in all cases.

surface	HCN		HNC			Barrier			
	R	r	R	r	V	γ	R	r	V
Boman <i>et al</i> ^a	3.198	2.196	2.902	2.220	5202	1.2654	2.1849	2.2544	16945
VCVQZ	3.1888	2.1806	2.9003	2.2097	5262	1.3650	2.1595	2.2464	16754
VQZANO1	3.1879	2.1805	2.9020	2.2101	5284	1.3522	2.1687	2.2463	16784
VQZANO2	3.1857	2.1789	2.9005	2.2085	5275	1.3347	2.1826	2.2425	16819
VQZANO+	3.1855	2.1785	2.9003	2.2081	5281	1.3338	2.1828	2.2421	16798
Expt. ^b	3.1869	2.1792	2.8979	2.2089	-	-	-	-	-
Expt. ^c	3.1871	2.1792	-	-	-	-	-	-	-

^a Potential surface of Bowman *et al* [116].

^b Experimental equilibrium bond lengths, determined by isotopic substitution [121, 120], errors are less than $10^{-4} a_0$.

^c Equilibrium bond lengths determined by spectroscopic fitting [136], authors do not quote errors.

Table 4.2: Summary of potential surfaces presented in this work. For details on all the surfaces see text.

Surface	Summary
VCVQZ	Fit to 243 CCSD(T)/cc-pCVQZ points.
VANO25	Fit to the 1527 points of Bowman <i>et al</i> [116], with energy $< 25\,000\text{ cm}^{-1}$.
VANO25S	Fit to the 1527 ‘shifted’ points of Bowman <i>et al</i> [116], with energy $< 25\,000\text{ cm}^{-1}$.
VQZANO1	Simultaneous fit of 243 CCSD(T)/cc-pCVQZ points and the 1527 ‘shifted’ points of Bowman <i>et al</i> [116], with energy $< 25\,000\text{ cm}^{-1}$.
VQZANO2	VQZANO1 surface morphed with 17 aug-cc-pCVQZ points at HNC geometries.
VQZANO+	VQZANO2 surface with relativistic and diagonal Born-Oppenheimer correction.

Chapter 5

Convergence Testing and Preliminary Calculations.

The DVR3D suite of programs was developed by Tennyson and co-workers [122, 123], to calculate rotational vibrational wavefunctions, eigenvalues, line frequencies and intensities and spectra of triatomic molecules. DVR3D has been successfully used to calculate extensive rotation-vibration linelists for H_2O [153] and H_3^+ [154]. It uses the Discrete Variable Representation (DVR), a grid based technique in conjunction with the Sutcliffe and Tennyson approach, see chapter 2. In this chapter I present convergence testing of the basis set that will be used for the full HCN/HNC linelist. I also outline the changes to the DVR3D suite, including parallelisation and optimisation, that were made during the course of the project. Finally I present some preliminary nuclear motion calculations performed with the DVR3D suite and the VQZANO+ PES and μQZ DMS, see chapter 4.

5.1 Convergence Testing of Input Parameters for DVR3D Suite.

The DVR3D suite is a set of programs for performing nuclear motion calculations on triatomics. Among these DVR3D modules are DVR3DRJZ, ROTLEV3, DIPOLE3 and SPECTRA, which are used in this work. The whole suite was reported in [122, 123]. A description of the functions of these four modules of the suite is given in section 2.7. Briefly the functions performed by these program modules are as follows.

DVR3DRJZ calculates vibrational wavefunctions, the starting point for the full rovibrational wavefunctions.

Table 5.1: DVR3D Input Parameters.

Parameter	function
NPNT1	Number of radial DVR points in the R_1 co-ordinate.
NPNT2	Number of radial DVR points in the R_2 co-ordinate.
NALF	Number of angular DVR points.
MAX3D	Maximum size of the 3 dimensional Hamiltonian matrix.
r_e	The equilibrium distance of the Morse-like radial basis functions.
D_e	The dissociation energy of the Morse-like radial basis functions.
ω_e	The oscillator frequency of the Morse-like radial basis functions.

ROTLEV3 performs the rotational step of the two step variational calculation, building on the wavefunctions from the DVR3DRJZ step. It outputs the full rovibrational wavefunctions and eigenvalues, for the specified value of J.

DIPOLE performs the integration to calculate the dipole transition strengths for lines that are not rigorously dipole forbidden transitions. It uses wavefunctions from ROTLEV3 and requires a dipole surface.

SPECTRA Calculates absorption or emission line frequencies and strengths and also a partition function at a given temperature. This allows the generation of synthetic spectra. Input of line frequencies and transition dipoles are taken from DIPOLE. For the calculation of a partition function energy levels are read in from ROTLEV output.

There is a choice of input parameters in the DVR3DRJZ and ROTLEV3 suites. These input parameters allow the selection of the size of the basis set, the basis function parameters and the level truncation of the matrices. These parameters determine the level of convergence of the calculation and effect the computational load of the calculation. A list of these parameters and their function is given in table 5.1.

The variational principle is used to converge the basis set and basis function parameters, see section 2.7. The parameters are adjusted to minimise the eigenvalues and hence obtain the best estimate for the converged basis.

5.1.1 Parameters of DVR3DRJZ

There are several parameters in the DVR3D program which effect the level of convergence and quality of the vibrational wave functions. These parameters are discussed here.

The number of grid points in the radial r and R co-ordinates is determined by the

parameters NPNT1 and NPNT2. The size of the angular basis is given by the parameter NALF. The parameters for the radial, Morse oscillator, basis functions are r_e , the equilibrium distance, D_e the dissociation energy and ω_e the harmonic frequency. Finally, MAX3D is the size of the three dimensional Hamiltonian.

No work on HCN/HNC using DVR3D has previously taken place. Therefore for the parameters $r_e(R)$ and $r_e(r)$ the equilibrium distances of HCN taken from Herzberg [156] were used. For the parameters $D_e(R)$ and $D_e(r)$ values of dissociation energy of the diatomics CH and CN were taken from Herzberg [155]. The values of these parameters are: $r_e(R) = 1.794 \text{ \AA}$, $r_e(r) = 1.157 \text{ \AA}$, $D_e(R) = 3.47 \text{ eV}$ and $D_e(r) = 6.05 \text{ eV}$. A starting point, taken from Viti [153] used for water, of $\omega_e = 0.007$ was used for both R and r co-ordinates. Each parameter was then adjusted to minimise the energy eigenvalues, in keeping with the variational principle.

The computational time, disk space and memory requirements increase linearly with NPNT1, NPNT2 and NALF. The disk space and memory requirements increase with the square of MAX3D and the runtime increase with the cube of MAX3D. However the quality of the convergence also increases with these parameters. The choice of these parameters is of utmost importance and is a matter of optimising the quality of the calculation to available computer resources and time limitations. Calculations were performed with various grid sizes and values of MAX3D to find the optimum values of these parameters, the final values of these parameters are quoted in table 5.6. To demonstrate the convergence of the grid size parameters calculations for J=0 vibrational states have been performed at 3 equally spaced values of these parameters, only one parameter was changed from those in table 5.6 at a time. The values of the parameters were $NPNT2 = 30, 35, 40$, $NPNT1 = 16, 21, 26$, $NALF = 45, 50, 55$ and $MAX3D = 2000, 2250, 2500$. The results are displayed graphically in figures 5.1, 5.2, 5.3 and 5.4 and summarised in tables 5.2, 5.3, 5.4 and 5.5. The figures plot the energy difference between energy eigenvalues calculated with the basis given in table 5.6 and with the parameter in question taking one of the test values that I have quoted above.

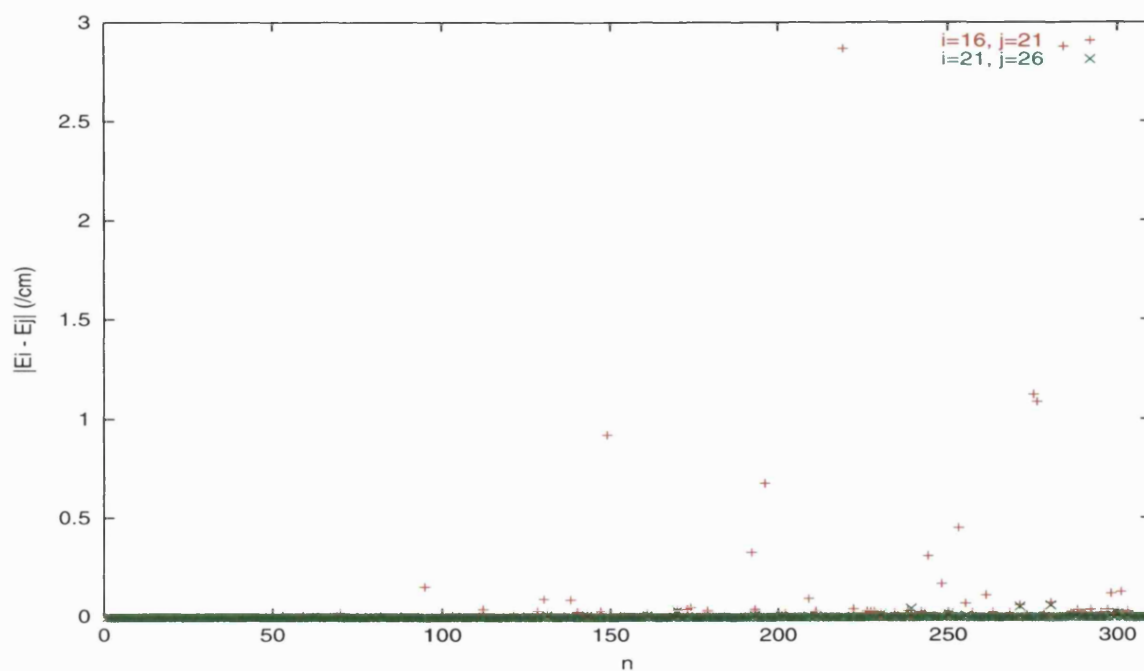


Figure 5.1: Figure illustrating convergence with NPNT1. Red crosses are the energy difference of the n^{th} energy level calculated with 16 and 21 points in the r co-ordinate. Likewise green crosses are energy difference of the n^{th} energy level calculated with 21 and 26 points.

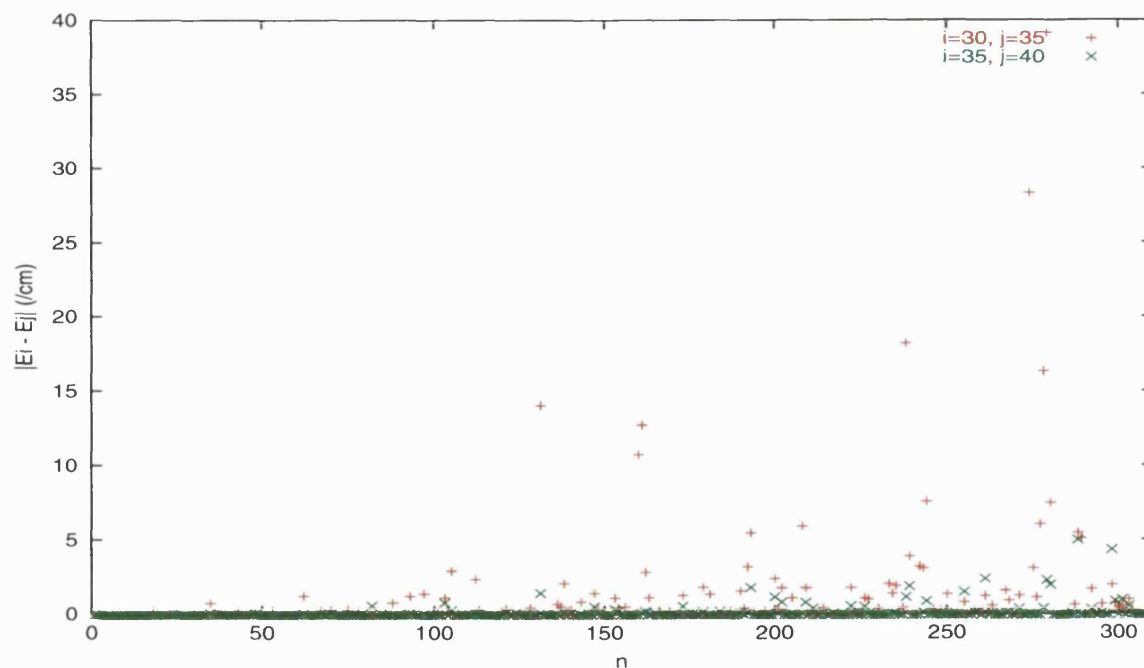


Figure 5.2: Figure illustrating convergence with NPNT2. Red crosses are the energy difference of the n^{th} energy level calculated with 30 and 35 points in the R co-ordinate. Likewise green crosses are the energy difference of the n^{th} energy level calculated with 35 and 40 points.

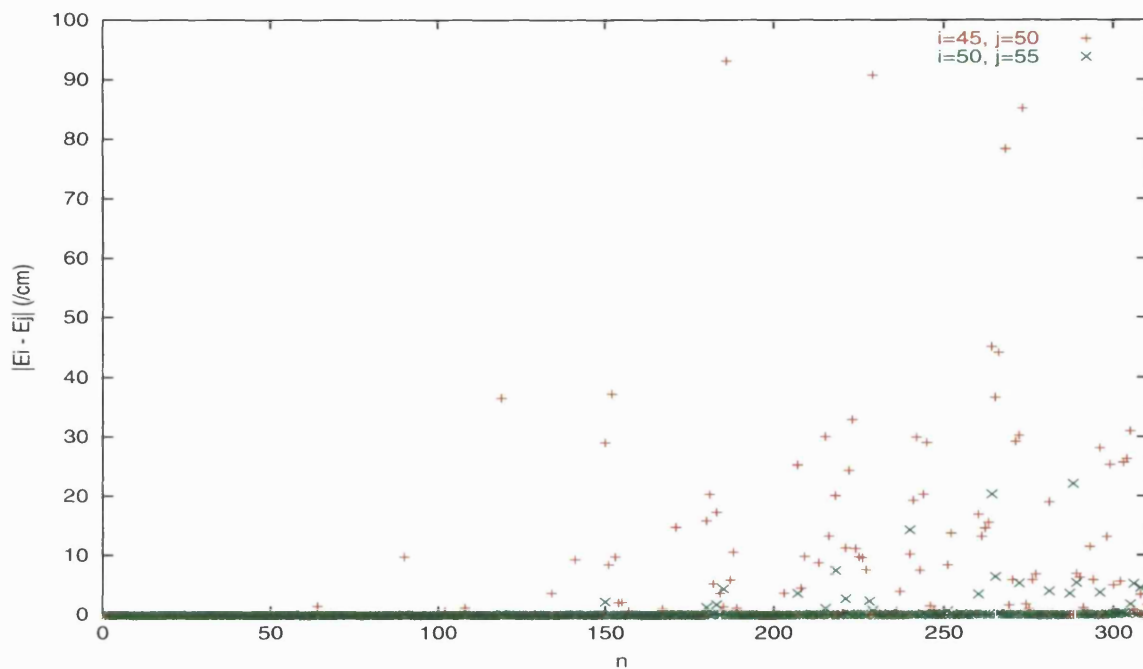


Figure 5.3: Figure illustrating convergence with NALF. Red crosses are the energy difference of the n^{th} energy level calculated with 45 and 50 angular points. Likewise green crosses are the energy difference of the n^{th} energy level calculated with 50 and 55 points.

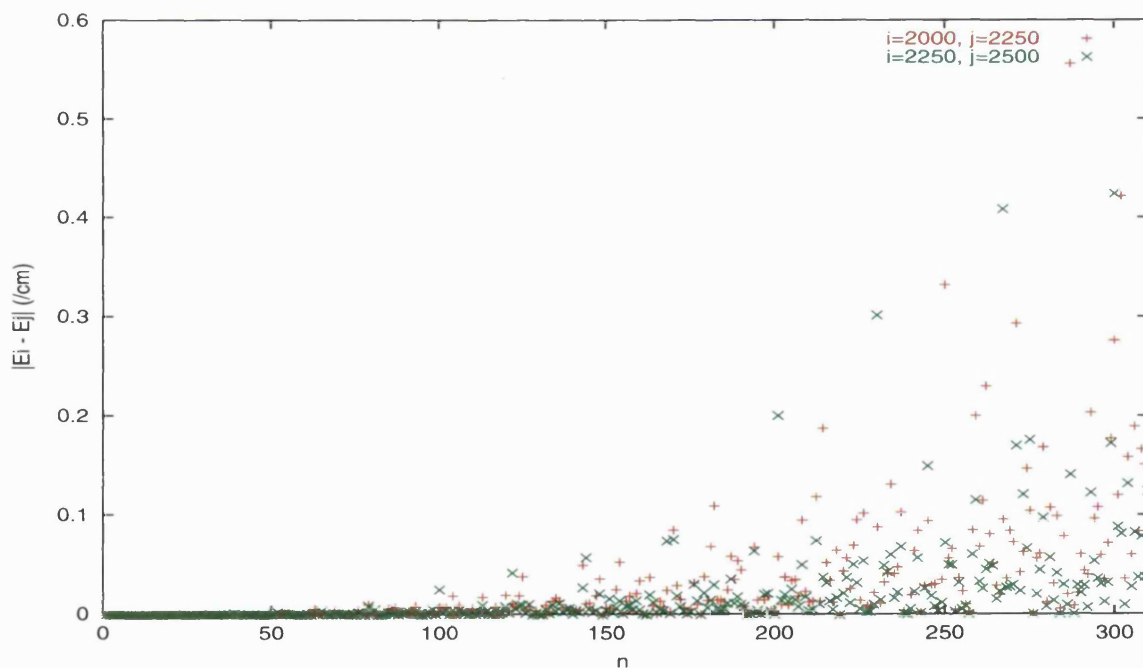


Figure 5.4: Figure illustrating convergence with MAX3D. Red crosses are the energy difference of the n^{th} energy level calculated with MAX3D=2000 and 2250. Likewise green crosses are the energy difference of the n^{th} energy level calculated with MAX3D=2250 and 2500.

Table 5.2: The mean energy difference (cm^{-1}) between the energy levels calculated with NPNT1=21 and those calculated with NPNT1=16, 21 and 26.

Max. Energy(cm^{-1})	N	mean ($E_{21} - E_{16}$)	mean ($E_{26} - E_{21}$)
10000	55	5.8×10^{-4}	5.7×10^{-5}
15000	175	1.0×10^{-2}	6.9×10^{-4}
18000	305	4.3×10^{-2}	1.6×10^{-3}

Table 5.3: The mean energy difference (cm^{-1}) between the energy levels calculated with NPNT2=35 and NPNT2= 30,40.

Max. Energy (cm^{-1})	N	mean ($E_{35} - E_{30}$)	mean ($E_{40} - E_{35}$)
10000	55	4.2×10^{-2}	7.0×10^{-3}
15000	175	4.1×10^{-1}	4.8×10^{-2}
18000	305	9.2×10^{-1}	1.4×10^{-1}

The energy eigenvalues for $J=0$ are converged to 0.05 cm^{-1} for levels below 15000 cm^{-1} and to 0.4 cm^{-1} for levels below 18000 cm^{-1} .

5.1.2 Parameters of ROTLEV3

The parameters to be converged in ROTLEV is primarily IBASS the size of the Hamiltonian in the second step of the calculation. If IBASS is too small, too few of the first step solutions are used in the second step. As a result the eigenvalues and eigenvectors will be poorly converged. States with high l proved to most sensitive to IBASS. In fact one of the problems encountered during the early stages of the calculation of the linelist was a result of poor rotational convergence. The calculated transition dipoles of transitions involving states with high values of l deviated from experiment in some cases by several orders of magnitude. To solve this problem a larger value of IBASS was used. The empirical equation for $\text{IBASS} = 400(J + 1)$ was found to be sufficient to converge calculations for energies below $18\,000 \text{ cm}^{-1}$ above the ZPE. For high J states the increasing size of IBASS from this equation becomes computationally expensive. However as the rotational energy increases with J , vibrational levels are 'pushed' beyond the energy cut off. At very high values of J , means that high l vibrational states such as $(0, 22^{22}, 0)$ are no longer in the region of the calculation. As a result fewer functions from the first step will be required

Table 5.4: The mean energy difference (cm^{-1}) between the energy levels calculated with NALF=50 and NALF: 45 and 50.

Max. Energy	N	mean ($E_{50} - E_{45}$)	mean ($E_{55} - E_{50}$)
10000	55	5.2×10^{-3}	1.9×10^{-3}
15000	175	9.8×10^{-1}	2.8×10^{-2}
18000	305	4.8	4.3×10^{-1}

Table 5.5: The mean energy difference (cm^{-1}) between the energy levels calculated with MAX3D=2250 and values of MAX3D=2000 and 2500.

Max. Energy	N	mean ($E_{2250} - E_{2000}$)	mean ($E_{2500} - E_{2250}$)
10000	55	3.0×10^{-4}	2.1×10^{-4}
15000	175	5.8×10^{-3}	4.3×10^{-3}
18000	305	3.1×10^{-2}	2.1×10^{-2}

and a smaller-than-expected value of IBASS will be required for convergence. This was tested for the $J = 20$ states,

5.2 Modifications to DVR3D Suite for This Work

Throughout the course of this work several changes were made to optimise and parallelise the DVR3D suite for this project. This included changing the diagonaliser, a minor output algorithm change to ROTLEV and attempts to parallelise the codes. The following discussion covers the adaption of the DVR3D suite to run on the 24 processor Miracle SGI Origin 2000 computer, at UCL's Hiperspace computing centre.

The architecture of the machine on which a calculation is to be performed is important when writing and optimising code. Therefore a brief description of the architecture of the Miracle SGI Origin 2000 computer follows. An SGI Origin 2000 (O2000) computer is what is known as a cache coherent - non uniform memory access (CC-NUMA) machine. In a CC-NUMA machine the computers memory appears to be shared and visible to all processors in the same way as in a uniform memory access (UMA) machine, see fig 5.5. However the memory bus of the UMA machine can only transport data to the processors at a certain rate. This leads to a slowdown in the memory access time when many processors are accessing the shared memory simultaneously. NUMA type machines were designed to partially overcome this problem, by distributing the memory across processors. An O2000

Table 5.6: Values used for th DVR3D Input Parameters.

Parameter	Preliminary Values	Final Values
Radial R Points (NPNT2)	40	35
Radial r Points (NPNT1)	25	21
Angular Points (NALF)	50	50
MAX3D	2250	2250
$r_e(r)$	$2.3 a_0$	$2.3 a_0$
$r_e(R)$	$3.2 a_0$	$3.2 a_0$
$D_e(r)$	$29.0 E_h$	$29.0 E_h$
$D_e(R)$	$5.0 E_h$	$5.0 E_h$
$\omega_e(r)$	$0.0105 E_h$	$0.0105 E_h$
$\omega_e(R)$	$0.004 E_h$	$0.004 E_h$

CC-NUMA machine can be thought of as a series of smaller UMA like machines, called nodes, joined together and sharing resources. Each of the nodes houses two processors, its own main memory, I/O ports and an 800 Mbytes/s NUMA2 interconnect, see fig 5.6. The nodes are joined together via the interconnect and a series of routers, see fig 5.7, to form a fast network of nodes. The resulting machine feels like an UMA machine in that any processor can access memory on any node. However there is the important advantage that each processor has its own “local” memory. That is the memory on its own node. Access to the local memory is fast because data does not need to be ported across the network. Memory on other nodes is called “remote” memory, access to remote memory may be slower than access to local memory and suffers the same machine load problems that occur in UMA machines. Ideally for a cc-NUMA machine each processor would have the data required for the calculation stored in its local memory. This is not always possible, for example a calculation may require more memory than is available in the local memory. In which case the data will be distributed across several nodes. Further problems can occur when the local memory is already being used by another process.

It is important to note that the theoretical maximum memory bandwidth is 800 Mbytes/s. Data cannot be moved from the memory faster than 800 Mbytes/s. If a calculation requires a memory transfer rate faster than 800 Mbytes/s, the rate at which the calculation is performed becomes limited by memory bandwidth. This problem was encountered during this project, see section 5.3.2.

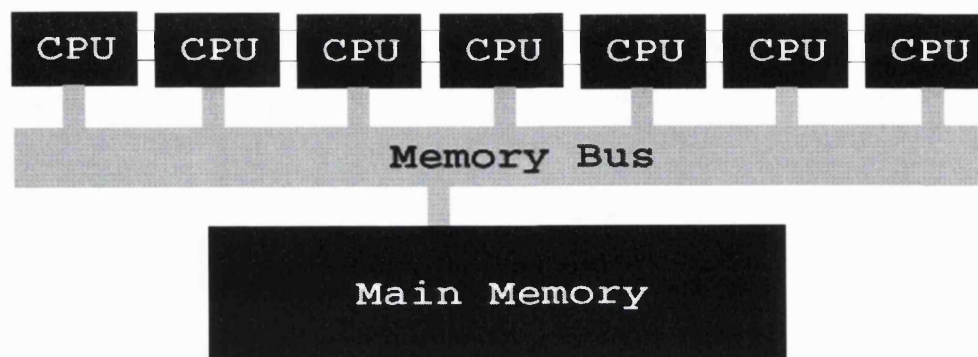


Figure 5.5: Figure illustrating the memory - processor architecture of a UMA multiprocessor computer.

All attempts to parallelise the codes in this project use the multiprocessor directives of the MIPSpro 7 Fortran 90 compiler [158]. These are based on the OpenMP Fortran application program interface (API) standard [159]. The OpenMP standard prescribes compiler directives that specify parallelism including environment variables and run time parallel options. When executed an OpenMP parallel program starts like a sequential single threaded program. This first thread is called the master thread and additional slave threads are generated when the program encounters a parallel region. One of the primary OpenMP directives used to parallelise the code in this project is: DOACROSS. This directive splits iterations of a DO loop between threads, thus sharing computational work load between threads. Importantly for effective parallisation all iterations of the loop must be:

- 1 Independent of the order in which they are performed
- 2 Must not write to the same variable or element of the same array.

There are also various optimizations that can be performed to increase the efficiency of the parallel code.

For the ideal parallel code the time taken for a calculation is inversely proportional

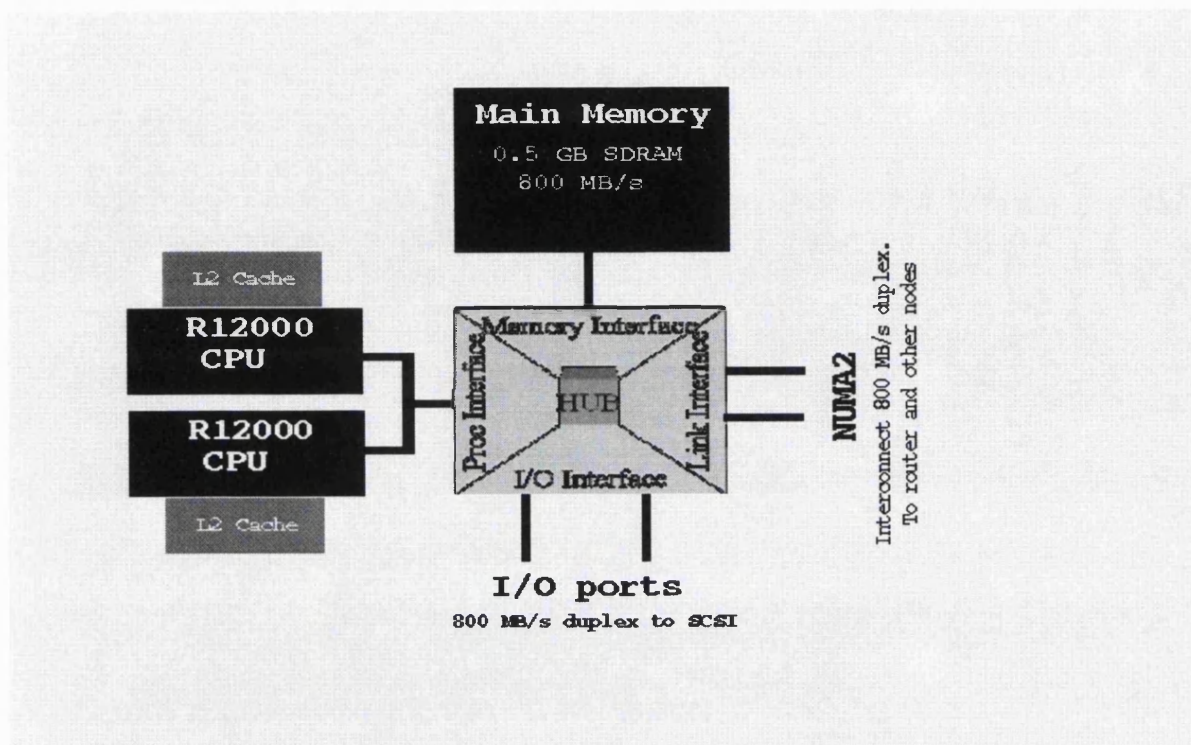


Figure 5.6: Figure illustrating the architecture on a node of the 'Miracle' SGI O2000 cc-NUMA computer.

to the number of CPU's used for the calculation, ie. $T_n = T_1/n$. For a real parallel calculation the efficiency of the parallelization is defined by: $E = \frac{T_1}{nT_n}$. The ideal case is $E = 1$, E usually takes a value of less than one, the closer that E is to one the more effective the parallelization.

5.3 Changes to DVR3DRJZ

DVR3DRJZ originally used the NAG diagonaliser F02ABF [160]. However for the Miracle SGI O2000 computer the serial NAG routines are poorly optimised. It was therefore desirable to use the LAPACK diagonaliser DSYEV [161], which has been well optimised by Silicon Graphics Inc. for their O2000 computers [162]. This resulted in a 25% reduction in runtime. DVR3DRJZ requires the least computer resources of the DVR3D suite. DVR3DRJZ typically uses $25 \times (J + 1)$ minutes of runtime and 55 Mbytes of RAM compared to more than 10 days runtime and 2.5 Gbytes of RAM for a large run of a serial version of DIPOLE3. It was therefore not necessary to parallelise DVR3DRJZ.

During the course of the calculation a bug in DVR3DRJZ at high J became evident.

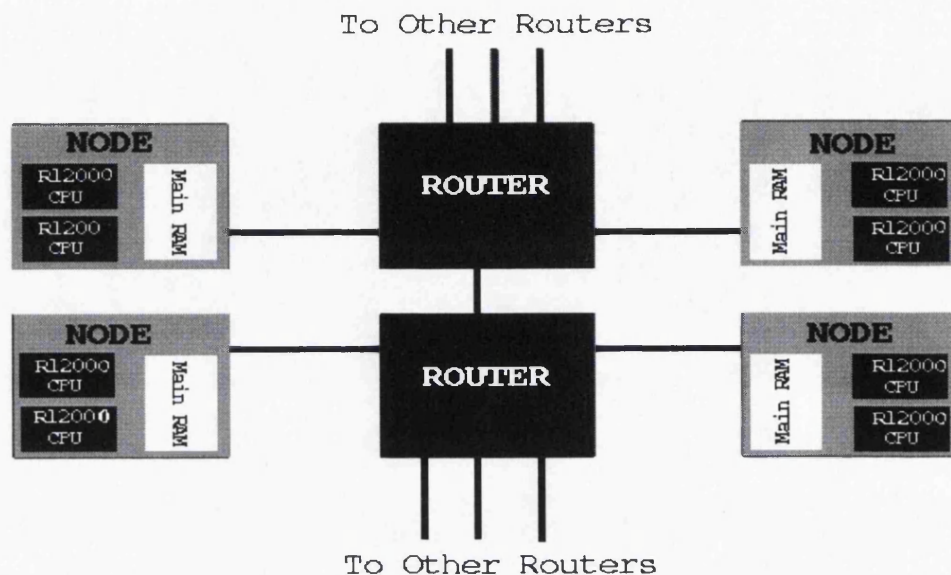


Figure 5.7: Figure illustrating the architecture of 4 interconnected nodes of a SGI O2000 cc-NUMA computer.

The bug was found in the JACOBI subroutine. This subroutine calculates the points and weights of the Gauss-Jacobi co-ordinates system. JACOBI calculates the roots (zero points) of the n^{th} order Jacobi polynomial in the $(-1, 1)$ segment. This is done by using a formula, given in ref [152], that finds the approximate, first guess, positions of the roots. The position of the roots are then improved by using the Newton-Raphson method. This method of finding the roots broke down at high J so that the incorrect points and weights of the Gauss-Jacobi quadrature were returned. The first phase of this method was modified. Instead of using approximate formulae a numerical technique was employed to find the first estimate for the positions of the roots. The numerical technique simply calculated the numerical value of the Jacobi polynomial over the $(0, 1)$ segment. The co-ordinates of the function were noted when it was closest to zero. These first guess co-ordinates are then improved by the Newton-Raphson method.

The modified JACOBI subroutine proved successful. All calculations beyond $J=33$ were performed using this modified routine.

5.3.1 Changes to ROTLEV3

The most time consuming step of the calculation is DIPOLE3. The runtime versus size of calculation tests that were performed indicated that for calculations of the size that were intended to be performed (4 million transitions at $J = 24 - 25$, $e - e$) would take of the order of 2 months. This runtime is too long to make the calculation practical. The same problem had been encountered during the calculation of a water linelist by Viti [153]. During the work of Viti, the algorithm of the old version of DIPOLE was optimised and I/O was reduced, the new code was called DIPOLE3.

This new version of DIPOLE was then implemented in the work of Viti [153] for symmeterised Radau co-ordinates and found to reduce runtime by as much as a order of magnitude. However DIPOLE3 takes input of the eigenvectors in a different format from that output by ROTLEV3, the version of ROTLEV used for Jacobi co-ordinates. The ROTLEV3 routine DSTORE controls the output of eigenvectors. DSTORE transforms the eigenvectors which are the solutions to the second step back to the original DVR basis and writes them to disk. DSTORE was rewritten so that it generates output in the format required for DIPOLE3B. The efficiency of DSTORE was also improved by reducing I/O and replacing repeated calls to a matrix-vector multiplier with a single call to a BLAS [163] matrix-matrix multiplier. The new and old formats of the output are shown in figure 5.3.1. When the new version of DIPOLE3 was run with the new format output from ROTLEV3 the runtime of DIPOLE was reduced from 2 months to about 6 days for the critical data, parallelisation reduced runtime further, see below.

5.3.2 Parallelisation and Optimisation of ROTLEV3

The runtime of ROTLEV3 for a $J = 20$ run including both e and f symmetry blocks (4000 levels) is about 10 days and uses up to 1 Gbytes of memory. To improve runtime an attempt was made to parallelise ROTLEV3. The routine SOLRT which sets up of the second step Hamiltonian was successfully parallelised as was the parallel matrix-matrix multiply BLAS routine in the DSTORE routine. However the NAG diagonaliser F02FJF, the most processor intensive step proved very difficult to parallelise.

F02FJF is called twice, once for each parity block which does not lend itself well to parallelisation. F02FJF makes multiple calls to a vector dot product routine and a vector-matrix multiplier, these calls take up the majority of time used by F02FJF. The vector-matrix multiplier was parallelised with some success. The vector dot product routine

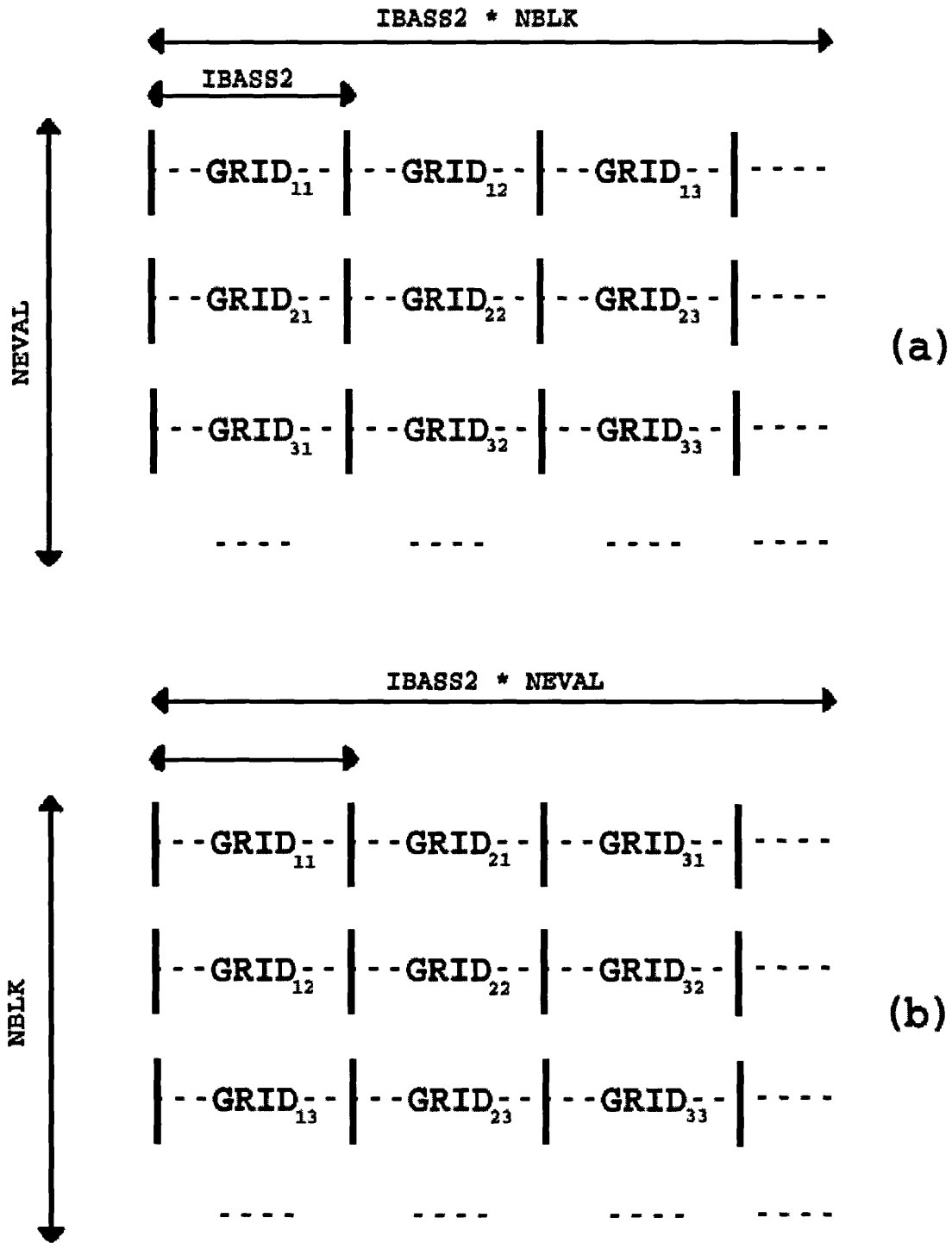


Figure 5.8: A schematic of the format of the output of: (a) the old version of ROTLEV3 and (b) the modified version of ROTLEV3. Here GRID is the DVR grid for a given level n and a given k block. IBASS2 is the total number of DVR points, NEVAL is the number of energy levels and NBLK is the number of K blocks. Each row is a row of floating point variables in the output.

cannot be parallelised, this is because efficient parallelisation depends upon the reuse of variables. When calculating the vector dot product each element of the vectors is used for one floating point multiply then discarded. This means data must be continually read from the memory. The speed of the calculation is therefore limited not by the processor speed but by memory bandwidth. Calculations limited by memory bandwidth do not gain from parallelisation. When run on 2 processors a full size calculation is parallel for about 25% of runtime, resulting in a modest reduction to about 80% of the serial runtime.

A further optimisation was a result of the well optimised parallel NAG SMP library functions [164]. The serial NAG library functions [160] are not optimised. So although the diagonalisation involving the F02FJF routine is not fully parallelised there was a considerable increase in efficiency to be had when compiling with the SMP NAG libraries. In fact runtime was nearly halved when using the SMP NAG libraries compared to using the serial NAG libraries.

Overall the runtime of ROTLEV3 for a $J = 20$ run including both e and f symmetry blocks (4000 levels) was reduced from about 10 days to less than 5 days.

5.3.3 Parallelisation of DIPOLE3B

DIPOLE3B is the longest step of the calculation, a serial version for a full size calculations uses 6 days runtime and 2.5 Gbytes core memory. DIPOLE3B must also be run three times for each value of J . This makes it desirable to reduce the runtime of DIPOLE3B, in this case via parallelisation.

For a full size calculation the TRANS routine of DIPOLE3 was found to consume almost 95% of run-time. TRANS is the main working routine in DIPOLE3, it evaluates and sums the contribution to the transition dipole at each grid point. Virtually all the run-time of TRANS is spent in the main loop. This loop integrates over the 2 sets of radial and the angular integration points, each time performing a rank one update on a matrix called $\mathbf{T}$. This matrix contains the sum of the contributions to the integration for each transition. An example of a rank one update is:

$$\mathbf{T} = a\mathbf{xy}^T + \mathbf{T} \quad (5.1)$$

Where $\mathbf{T}$ is an n by m matrix, a is a constant, $\mathbf{x}$ is an n -element vector and $\mathbf{y}^T$ is the transpose of the m -element vector $\mathbf{y}$.

The main loop of TRANS had to be rewritten before it could be parallelised. Each

Table 5.7: Wall clock time required by TRANS for $J = 0 \rightarrow 1e$ calculation.

Number of Processors	Time (s)	efficiency
1	258	-
2	140	0.92
3	101	0.85
4	73	0.88
8	38	0.84

iteration of the loop used the results of the previous iteration which were stored in the $\mathbf{T}$ matrix. To solve this problem each iteration of the loop had to be made independent of all other iterations. n matrices, one for each processor, of the same dimensions of the $\mathbf{T}$ matrix were defined. Each processor could then read and write exclusively to its own matrix. These matrices were then summed on completion of the loop to, find the final $\mathbf{T}$ matrix.

To test the efficiency of the parallelisation a full sized $J = 0e$ to $J = 1e$ calculation was performed on 1, 2, 3, 4 and 8 processors. This is a relatively short calculation compared to states with higher rotational excitation and requires only 600 Mbytes memory. The time spent in TRANS and all successive calls to subroutines is given in table 5.7.

For this test calculation $E \sim 0.88$ and the parallelisation overhead is about 13% . The TRANS function of DIPOLE3 in this case clearly benefits from parallelisation and looks to be scalable.

The much larger high J calculations take over 2 Gbytes of memory, more than 4 times the memory available on one node. As a consequence memory is distributed across several nodes. The time required by the calculation is then dependent upon the load on the machine and the distribution of data over the nodes. During the project it was found that 2 identical calculations can have run times that are different by up to a factor of two. This causes problems when benchmarking the parallel calculations. The effects of which can be seen in table 5.8, which shows the total runtime as well as runtime taken by the TRANS subroutine for the $J = 27e \rightarrow 27f$ transitions. This calculation requires ~ 2 Gbytes.

Clearly the parallelisation is not as scalable or efficient as in the $J = 0e \rightarrow 1f$ test case above. None the less the parallelisation is of clear benefit, reducing run time appreciably. A run that would take 4.5 days in serial, now takes 1.06 days on 10 processors.

Table 5.8: Wall clock time required for $J = 27e \rightarrow 27f$ calculation.

Number of Processors	Time in TRANS (H)	Total Time (H)
1	100.6	108.0
2	68.7	76.0
4	40.4	47.7
8	25.2	32.5
10	18.2	25.5

5.3.4 Update of and Changes to SPECTRA

SPECTRA takes the transition frequencies and transition dipoles from the dipole output, sorts them in frequency order and generates a spectrum. The subroutine SORTSP that sorts the transitions into frequency order is by far the most time consuming. Many of the transitions in the linelist may be of interest to the user. For example a line may be too weak or out of the relevant frequency range. So a block of code that selects transitions on minimum and maximum frequency, energy and transition dipole was included. This allows the user to select the region of interest and cuts runtime dramatically. The original version of spectra used the NAG [160] sorting routines M01DEF and M01EAF. These routines sort a given column of a two dimensional floating point array into the numerical order. Much of the data in the linelist is of integer type, for example the parity and the J quantum number. The integer data had to be converted to floating point variables then sorted and converted back to integers. SPECTRA was modified to use DPSORT and its associated freeware sorting routines [165]. These routines allow sorting of both integer and floating point variables. Finally SPECTRA was debugged and updated to FORTRAN90. This allowed for dynamic memory allocation to be used for the main arrays and made the routine GTMAIN, which assess the maximum memory need and sets up the main arrays, redundant.

5.4 Preliminary Nuclear Motion Calculations.

Before starting an extensive calculation of a linelist it is important to determine the accuracy of the potential surfaces that are to be used in the calculation. The best way that the accuracy of the surfaces can be determined is by performing some preliminary test calculations. In this section I present preliminary calculations of some rotational-

vibrational energy levels, lines and transition dipoles these are compared with experimental data and earlier *ab initio* data. The DVR3D suite of programs (see section 2.7) [122] was used to perform all the calculations in this section. These preliminary calculations took place before the basis, see section 5.1, was optimised to 18000 cm^{-1} . Therefore the basis used for these calculations is slightly larger and less well optimised than in section 5.1. This basis uses $NPNT1 = 40$, $NPNT2 = 25$ and $NALF = 50$. The full list of input parameters is given in table 5.6 in the "preliminary values" column.

5.4.1 HCN and HNC Band Origins.

All ($J = 0$) vibrational band origins for HCN and HNC states below $12\,400\text{ cm}^{-1}$ relative to the HCN zero point energy, have been calculated. These were calculated from the *ab initio* VQZANO x family of surfaces (where $x = 1, 2, +$. See chapter 4) and also the Bowman *et al* PES [116]. The results are reported in Tables 5.9 and 5.10, also quoted in these tables are the results calculated by Bowman *et al* [116] using their surface and experimentally determined band origins.

The HCN band origins calculated using the Bowman *et al* surface with the DVR3D suite agree, in general, with the results quoted by Bowman *et al* in their paper [116] to within 0.5 cm^{-1} at energies upto $12\,400\text{ cm}^{-1}$. However for the HNC band origins there is a larger discrepancy between the two sets of data. For example there is a difference of the order of 3 cm^{-1} for the high HNC bending states and 20 cm^{-1} for the H-N stretch. In general the HNC band origins calculated using the DVR3D suite agree more closely with the available experimental data than do those calculated by Bowman *et al*. The level of agreement between the band origins calculated with the DVR3D suite and those calculated by Bowman *et al* confirms that our basis set is valid and well converged for the HCN eigenstates and also gives HNC band origins in better agreement with the available experimental data than the calculations of Bowman *et al*. In a recent paper Bowman *et al* [118] have recalculated the HCN and HNC band origins with their surface [116]. Their new calculations give HNC band origins which are different from their earlier HNC calculations. These new Bowman *et al* [118] band origins agree with the calculations with the Bowman *et al* [116] surface that were performed in this work.

The band origins calculated with the VQZANO x family of surfaces agree well with experiment, the HCN and HNC fundamentals agree to within 4 cm^{-1} except the $\nu_1(\text{HNC})$ fundamental, a special case (see section 4.2.1). The morphed VQZANO2 surface shows

an improvement over the unmorphed VQZANO1 surface, cutting the value of $E_{\text{obs}} - E_{\text{calc}}$ by 1/3, so clearly the morphing makes an important improvement of the VQZANO2 and VQZANO+ PES's over the VQZANO1 PES.

These HCN and HNC *ab initio* vibrational band origins are significantly closer to experiment than the *ab initio* vibrational band origins of Bowman *et al* , especially for the HNC band origins and the HCN levels containing excited CH stretch. The better agreement of these new HNC band origins again shows the need for using a larger electronic basis set for HNC geometries. For bending states with $\nu_2 < 8$, the results from our surfaces are closer to experiment than the band origins calculated by Bowman *et al* . However, for bending states with $\nu_2 \geq 8$ the VQZANO1 surface gives results that are of comparable accuracy to those of Bowman *et al* , but the VQZANO+ and VQZANO2 surfaces give vibrational band origins that are roughly 5 cm^{-1} further from the experimental values. This increase in error in our results is caused by the change in co-ordinates of the HCN minimum in the 3 point mapping, see section 4.2.2. There is some cancellation of error in the bend and CN stretch combination band origins of Bowman *et al* with $\nu_1 = 0$, $\nu_2 \geq 8$, $\nu_3 \geq 1$, this cancellation of error is not present in the results from the VQZANO+ surface. Overall due to the higher level of the electronic basis set and also the auxiliary corrections used for the VQZANO+ PES, band origins calculated with the VQZANO+ surface agree more closely with experiment than do band origins calculated with the surface of Bowman *et al* .

5.4.2 HCN and HNC Rotational Energy Levels.

The HCN and HNC $J = 1, 5, 10, 15, 20$ pure rotational states have been calculated with the VQZANO1 and VQZANO+ surfaces and the surface of Bowman *et al* [116], see Tables 5.11 and 5.12. At the time of calculation only the relatively low lying rovibrational states ($>9000 \text{ cm}^{-1}$) were of interest, hence to save computational time the rotational basis (IBASS) was truncated at a lower level ($100 \times (J + 1)$) than in the full, final calculations..

The rotational term values obtained for the VQZANO1 and VQZANO+ surfaces agree to within 0.5 cm^{-1} at $J = 20$ with the experimental values, where as the values obtained with the surface of Bowman *et al* deviate from experiment by an order of magnitude more. It is clear from this that the VQZANOx surfaces are far more accurate for rotational calculations than the surface of Bowman *et al* . Particularly notable is the improvement in the CN bond length in our calculations compared to those of Bowman *et al* , which is

reflected in this improved representation of the rotational motion.

The rotational levels of HCN and HNC calculated from the VQZANO+ PES show improvement over the levels calculated from the VQZANO1 PES. This improvement is caused by the remapping the critical points, one of the improvements in the VQZANO+ over the VQZANO1 PES.

Rovibrational energy levels for the fundamental bands of HCN and HNC have been calculated using the VQZANO+ surface and the surface of Bowman *et al*, see Tables 5.11 and 5.12. The obs-calc for these levels have been calculated and corrected for the known vibrational error, the rotational errors are, as for the pure rotational levels, less than 0.7 cm^{-1} for the $J = 20$ state. This small error makes the surface useful for spectroscopic line assignments and the obs-calc of the VQZANO+ is again an order of magnitude smaller than that of the surface of Bowman *et al*.

5.4.3 HCN and HNC Band Transition Dipoles.

Rovibrational wavefunctions were calculated with the DVR3D suite of programs using the VQZANO+ PES and also the Bowman *et al* [116]. The wavefunctions were then used to compute transition dipoles using the DVR3D suite with the μQZ dipole surface and the μAQCC dipole surface which is a fit to the dipole points of Jakubetz and Lan [117] (see section 4.4.1). The calculations with the VQZANO+ wave functions and the μQZ dipole surface used transitions with $0 \leq J < 4$ and all other calculations used transitions with $J = 0$ and $J = 1$.

Jørgensen *et al* [54] computed, at the CASSCF level with a (C/N,H)= (5s4p2d,3s1p) basis set the frequencies and integrated band intensities of 8 HCN bands. We have calculated the band transition dipole for these 8 lines and also the (02²0)-(01¹0) band for comparison, using rotational transitions with $0 \leq J < 4$, see Tables 5.13 and 5.14.

On the whole the dipole strengths calculated using wavefunctions from the VQZANO+ surface and wavefunctions from the surface of Bowman *et al* along with the μAQCC dipole surface agree, but for the 3 quanta of bend overtone the two results differ by a factor of three. Both results are roughly an order of magnitude smaller than experiment. In general the results using the wavefunctions from the VQZANO+ surface agree better with experiment than the results using wave functions from the surface of Bowman *et al*.

Jakubetz and Lan experienced problems at small to large displacements from the C-N equilibrium near the HCN minimum caused by the inapplicability of the single reference

SCF method in this region. Consequently they left out their dipole points in this region and used an extrapolation from higher angles, in their surface, for the near-linear HCN geometries. Jakubetz in a private communication [115] states that intensities calculated from their surface will be strongly fit dependent for the HCN C-N stretch modes. The problem shows up in the dipole strengths of the C-N stretch fundamental and the H-C and C-N stretch combination calculated with the μ AQCC dipole surface, these bands have large errors.

The results using the μ QZ dipole surface compare well with experiment, especially the states involving a transition of the HC stretch (ν_1), and are generally within experimental error. These results are generally closer to the experimental values than the earlier works of Jørgensen *et al* [54] and Jakubetz and Lan [117] as would be expected from the higher level of theory used to calculate our dipole points. It must also be noted that the μ AQCC dipole surface is a fit to the dipole points of Jakubetz and Lan and not the same surface as used for their calculations in their paper. So differences between dipole strengths calculated with the μ AQCC dipole surface and those calculated by Jakubetz and Lan is to be expected.

Overall from the above arguments the μ QZ surface is superior to the surface of Jakubetz and Lan and the μ AQCC surface.

5.5 Conclusion: The Surfaces to be Used.

Wu *et al* [119] have fitted a global HCN/HNC potential energy surface (PES) to experimental data to create a PES which can reproduce known experimental vibrational energy levels to within 1 cm^{-1} . However although spectroscopically fitted surfaces reproduce known experimental data to high accuracy, they tend to extrapolate high lying energy levels outside the fitted region far more poorly than do *ab initio* surfaces, see section 3.8.

There are currently three *ab initio* semi-global HCN/HNC PES available these are the ANO/CCSD(T) PES of Bowman *et al* [116], the *ab initio* surface of Varandas and Rodrigues [173] and the VQZANO+ PES covered in chapter 4. The VQZANO+ PES includes relativistic and adiabatic corrections, which are often neglected when constructing an *ab initio* PES. The PES of Varandas and Rodrigues [173] is a fit to the electronic potential points of Bowman *et al* [116] at lower energies and to new *ab initio* FVCAS/TZV2P high energy electronic points. Consequently the surface of Varandas and Rodrigues [173] is relatively poor in the low energy region, see section 3.7, which is of interest in this project.

Vibrational energy level calculations with the VQZANO+ PES give stretching band origins that more closely match experiment than do the stretching band origins calculated with the Bowman *et al* PES [116] and the bending band origins are of a comparable level of accuracy, see above. The positions of the HCN and HNC minima of the VQZANO+ PES are considerably closer to experimental equilibrium bond lengths, determined by isotopic substitution [120, 121], than those of the Bowman *et al* PES. This results in the VQZANO+ PES giving a better representation of the molecules rotational motion than the Bowman *et al* PES see above. Overall the VQZANO+ PES is in general superior to the PES of Bowman *et al* , as a result we use the VQZANO+ PES for the calculation of the linelist.

There are three semi-global dipole moment surfaces (DMS) available these are the TZP/AQCC DMS of Jakubetz and Lan [117], the aug-cc-pCVTZ/CCSD(T) DMS of Bowman *et al* [118] and cc-pCVQZ/CCSD(T) DMS (μ QZ) see chapter 4. The DMS of Jakubetz and Lan [117] was calculated with the smallest basis of these three DMS, the intensities calculated with it compare with experiment less favorably than do our calculations with the μ QZ DMS, see above. The DMS of Bowman *et al* [118], uses fewer electronic points and a smaller basis than the μ QZ DMS [23]. The μ QZ surface as a result is the best available DMS and the one which will be employed for the calculation of the linelist.

Table 5.9: HCN $l = 0$ and $J = 0$ pure vibrational band origins (cm^{-1}), relative to HCN zero point energy. Calculated with various potential surfaces, and compared to experimental band origins.

ν_1	ν_2	ν_3	VQZANO+	VQZANO2	VQZANO1	ANO ^a	Bowman ^b	Expt. ^c
0	0	0	3481.46 ^d	3482.16 ^d	3481.69 ^d		3477.4 ^d	
0	2	0	1414.92	1415.06	1414.24	1418.93	1418.9	1411.42
0	0	1	2100.58	2100.93	2100.93	2090.44	2090.3	2096.85
0	4	0	2801.46	2801.80	2800.14	2812.64	2812.5	2802.96
1	0	0	3307.75	3308.61	3308.71	3334.29	3334.1	3311.48
0	2	1	3510.99	3511.39	3510.58	3507.53	3507.4	3502.12
0	6	0	4176.24	4176.80	4174.05	4178.28	4178.0	4174.61
0	0	2	4181.45	4182.14	4182.14	4161.52	4161.5	4173.07
1	2	0	4686.29	4687.24	4687.08	4703.44	4703.4	4684.31
0	4	1	4891.76	4892.26	4890.61	4899.94	4899.9	4888.00
1	0	1	5394.43	5395.67	5395.77	5399.46	5399.4	5393.70
0	8	0	5537.76	5538.56	5534.28	5532.49	5532.3	5525.81
0	2	2	5586.50	5587.13	5586.32	5570.53	5570.5	5571.89
1	4	0	6033.72	6034.83	6034.75	6054.14	6054.0	6036.96
0	0	3	6242.42	6243.43	6243.43	6211.20	6211.4	6228.60
0	6	1	6260.59	6261.22	6258.49	6256.65	6256.5	6254.38
2	0	0	6513.50	6515.23	6515.43	6553.30	6553.2	6519.61
1	2	1	6768.51	6769.74	6769.57	6765.70	6765.5	6761.33
0	10	0	6879.60	6880.72	6874.10	6873.54	6873.5	6855.53
0	4	2	6960.99	6961.60	6959.97	6958.61	6958.5	6951.68
1	6	0	7369.18	7370.47	7370.39	7390.45	7390.3	—
1	0	2	7461.60	7463.19	7463.28	7445.33	7445.7	7455.42
0	8	1	7617.24	7618.06	7613.76	7600.77	7600.6	—
0	2	3	7641.28	7642.09	7641.28	7609.09	7609.4	—
2	2	0	7855.84	7857.60	7858.08	7878.95	7878.8	7853.51
1	4	1	8110.25	8111.54	8111.44	8115.45	8115.2	8107.97
0	12	0	8197.55	8199.04	8188.72	8185.52	8185.3	—

ν_1	ν_2	ν_3	VQZANO+	VQZANO2	VQZANO1	ANO ^a	Bowman ^b	Expt. ^c
0	0	4	8283.37	8284.68	8284.68	8238.58	8239.7	—
0	6	2	8323.52	8324.18	8321.47	8308.36	8308.3	—
2	0	1	8584.74	8586.88	8587.08	8595.58	8595.9	8585.58
1	8	0	8691.67	8693.18	8692.59	8710.37	8710.3	—
1	2	2	8830.27	8831.73	8831.55	8805.93	8806.2	8816.00
0	10	1	8954.47	8955.52	8948.84	8935.01	8935.0	—
0	4	3	9009.00	9009.68	9008.06	8990.40	8990.5	8995.22
2	4	0	9164.08	9165.95	9167.39	9188.94	9188.5	—
1	6	1	9440.12	9441.50	9441.36	9441.46	9441.3	—
0	14	0	9488.54	9490.47	9474.37	9470.37	9470.3	—
1	0	3	9508.91	9510.83	9510.92	9472.13	9474.5	9496.44
3	0	0	9619.29	9621.88	9622.16	9668.37	9668.3	9627.09
0	2	4	9674.67	9675.46	9671.22	9623.28	9624.3	—
0	8	2	9675.25	9676.17	9675.33	9644.92	9644.9	—
2	2	1	9922.92	9924.98	9925.45	9917.90	9918.1	9914.4
1	10	0	9993.95	9995.76	9993.57	10010.05	10010.0	—
1	4	2	10165.6	10167.0	10166.9	10152.20	10152.3	—
0	12	1	10266.4	10267.8	10257.3	10237.97	10237.7	—
0	0	5	10304.1	10305.7	10305.7	10243.42	10246.8	—
0	6	3	10364.9	10365.6	10362.9	10333.99	10334.0	—
2	6	0	10460.5	10462.6	10465.0	10489.25	10488.9	—
2	0	2	10636.7	10639.2	10639.4	10621.68	10623.7	10631.4
0	16	0	10749.7	10752.1	10727.4	10724.17	10724.2	—
1	8	1	10758.0	10759.6	10758.8	10755.19	10755.3	—
1	2	3	10871.1	10872.7	10872.5	10824.09	10826.4	—
3	2	0	10925.3	10927.8	10928.9	10951.19	10951.0	—
0	10	2	11006.5	11007.5	11000.8	10971.42	10971.4	10974.2
0	4	4	11035.7	11036.4	11034.8	10996.83	10997.7	11015.9
2	4	1	11225.9	11227.9	11229.4	11229.27	11229.2	—
1	12	0	11271.7	11273.9	11268.2	11279.66	11279.5	—

ν_1	ν_2	ν_3	VQZANO+	VQZANO2	VQZANO1	ANO ^a	Bowman ^b	Expt. ^c
1	6	2	11489.4	11490.8	11490.6	11467.23	11467.5	—
0	14	1	11536.1	11538.1	11535.0	11514.62	11514.6	—
1	0	4	11549.6	11551.4	11550.3	11479.25	11487.4	11516.6
3	0	1	11672.8	11675.9	11676.2	11685.14	11686.9	11674.5
0	2	5	11688.1	11689.1	11688.3	11614.36	11617.6	—
0	8	3	11710.1	11710.8	11706.6	11664.17	11664.3	—
2	8	0	11744.5	11746.6	11751.8	11770.27	11770.2	—
2	2	2	11969.9	11967.9	11972.6	11940.00	11939.9	—
0	18	0	11977.7	11980.8	11944.0	11937.68	11939.8	—
1	10	1	12055.7	12057.5	12055.1	12051.44	12051.4	—
1	4	3	12192.5	12194.9	12197.0	12164.52	12166.6	—
3	4	0	12200.6	12202.2	12202.7	12222.00	12221.5	—
0	0	6	12304.5	12306.3	12302.4	12225.94	12233.8	—
0	12	2	12311.7	12313.0	12306.3	12265.85	12265.7	—
0	6	4	12382.0	12385.3	12387.7	12334.13	12334.8	—

^a Band origins calculated with the DVR3D suite using the surface of Bowman *et al* [116].

^b Calculations performed by Bowman *et al* [116].

^c Refs [83, 149, 138, 147, 148].

^d The HCN zero point energy for given surface.

Table 5.10: HNC $l = 0$ and $J = 0$ pure vibrational band origins (cm^{-1}), relative to HNC zero point energy. Calculated with various potential energy surfaces and compared to experiment.

ν_1	ν_2	ν_3	VQZANO+	VQZANO2	VQZANO1	ANO ^a	Bowman ^b	Expt. ^c
0	0	0	5185.64 ^d	5180.27 ^d	5183.40 ^d	5024.49 ^d	5023.2 ^d	—
0	2	0	941.917	942.541	942.601	927.20	919.9	—
0	4	0	1903.10	1904.61	1904.67	1899.80	1895.5	—
0	0	1	2024.95	2025.29	2025.54	2027.39	2024.6	2023.88
0	6	0	2834.81	2837.40	2837.32	2859.20	2858.8	—
0	2	1	2955.05	2955.92	2956.24	2937.69	2929.2	—
1	0	0	3665.10	3666.55	3672.35	3618.04	3599.1	3652.68
0	8	0	3759.86	3763.67	3763.16	3794.30	3794.7	—
0	4	1	3902.41	3904.11	3904.45	3898.86	3892.2	—
0	0	2	4029.21	4029.89	4030.44	4029.50	4024.4	—
1	2	0	4558.15	4560.11	4567.20	4523.08	4507.1	—
0	10	0	4679.69	4684.95	4683.85	4726.57	4727.3	—
0	6	1	4820.95	4823.73	4823.90	4834.28	4832.8	—
0	2	2	4946.74	4947.86	4948.47	4921.97	4912.6	—
1	4	0	5469.23	5471.98	5480.24	5451.33	5440.7	—
0	12	0	5568.34	5575.51	5573.89	5635.18	5638.0	—
1	0	1	5676.51	5678.3	5684.39	5635.18	5628.7	5664.85
0	8	1	5736.39	5740.4	5740.12	5753.08	5752.6	—
0	4	2	5879.59	5881.49	5882.1	5870.62	5862.4	—
0	0	3	6012.87	6013.89	6014.76	6005.79	5999.1	—
1	6	0	6354.07	6358.05	6354.99	6344.84	6337.0	—
0	14	0	6404.38	6413.83	6411.88	6479.60	6482.6	—
1	2	1	6558.72	6561.02	6566.03	6532.09	6518.2	—
0	10	1	6646.85	6652.35	6651.51	6677.07	6676.6	—
0	6	2	6784.63	6791.92	6788.03	6783.59	6781.6	—
0	2	3	6917.05	6918.4	6919.33	6881.19	6871.3	—
2	0	0	7189.47	7192.43	7199.25	7138.04	7116.7	7171.41

0	16	0	7199.11	7208.06	7205.92	7277.80	7279.9	–
1	8	0	7226.47	7231.44	7240.87	7232.70	7225.5	–

^a Band origins calculated with the DVR3D suite using the Bowman *et al* PES [116].

^b Calculations performed by Bowman *et al* [116] on their surface..

^c Refs [150, 139].

^d The energy of the HNC (0,0,0) state relative to the HCN zero point energy.

Table 5.11: Calculated HCN rotational-vibrational energy levels (cm^{-1}), relative to the zero point energy of HCN.

$(\nu_1 \nu_2^l \nu_3)$	J	VQZANO+	VQZANO1	ANO ^a	Expt. ^b	obs-calc ^c _{vqzано+}	obs-calc ^d _{ANO}
(00 ⁰ 0)	1	2.959	2.954	2.919	2.956	-0.0005	0.037
	5	44.39	44.31	43.79	44.32	-0.08	0.53
	10	162.72	162.44	160.53	162.54	-0.18	2.0
	15	354.94	354.32	350.16	354.58	-0.36	4.4
	20	620.93	619.87	612.56	620.34	-0.59	7.8
(01 ^{1e} 0)	1	718.85		718.30	714.94	(-3.91) ^e	(-3.36) ^e
	5	760.27		759.16	756.29	-0.06	0.49
	10	878.60		875.87	874.51	-0.18	2.0
	15	1070.80		1065.45	1066.51	-0.38	4.4
	20	1336.77		1327.78	1332.22	-0.64	7.8
(00 ⁰ 1)	1	2103.52		2093.34	2099.78	-0.01	0.03
	5	2144.67		2133.98	2140.87	-0.07	0.48
	10	2262.21		2250.08	2258.28	-0.20	1.8
	15	2453.14		2438.65	2449.01	-0.40	4.0
	20	2717.33		2699.58	2712.93	-0.67	6.9
(10 ⁰ 0)	1	3310.68		3337.19	3314.41	0.00	0.03
	5	3351.83		3377.80	3355.49	-0.07	0.50
	10	3469.34		3493.80	3472.88	-0.19	1.9
	15	3660.23		3682.23	3663.56	-0.40	4.14
	20	3924.38		3942.98	3927.42	-0.69	7.25

^a The rovibrational levels calculated with the DVR3D suite using the Bowman *et al* [116] PES.

^b Experimental data [111, 112, 147]

^c Obs-calc for VQZANO+ PES results corrected for the vibrational error.

^d Obs-calc for Bowman *et al* [116] PES results corrected for the vibrational error.

^e The lowest rotational state for (01^{1e}0), taken as vibrational error.

Table 5.12: Calculated HNC rotational-vibrational energy levels (cm^{-1}), relative to HNC (0,0,0)

$J=0$ state.

$(\nu_1\nu_2^l\nu_3)$	J	VQZANO+	VQZANO1	ANO ^a	Expt. ^b	obs-calc ^c _{vqzано+}	obs-calc ^d _{ANO}
(00 ⁰ 0)	1	3.021	3.025	2.997	3.042	0.02	0.045
	5	45.36	45.29	44.95	45.36	0.00	0.41
	10	166.29	166.02	164.80	166.29	0.00	1.5
	15	362.72	362.11	359.45	362.72	0.00	3.3
	20	634.52	633.45	628.80	634.50	0.02	5.7
(01 ^{1e} 0)	1	468.15		464.86	465.74	(-2.41) ^e	(0.88) ^e
	5	510.48		506.81	508.07	0.00	0.38
	10	631.38		626.65	628.97	0.00	1.4
	15	827.77		821.30	825.36	0.00	3.2
	20	1099.50		1090.64	1097.09	0.00	5.6
(00 ⁰ 1)	1	2027.95		2030.37	2026.86	-0.02	0.00
	5	2069.98		2072.04	2068.88	-0.03	0.35
	10	2190.05		2191.10	2188.92	-0.06	1.33
	15	2384.92		2384.48	2383.89	0.04	2.92
	20	2654.92		2652.06	2653.66	-0.19	5.11
(10 ⁰ 0)	1	3667.97		3621.02	3655.66	0.11	0.00
	5	3710.13		3662.66	3697.72	0.01	0.42
	10	3830.34		3781.64	3817.85	-0.07	1.57
	15	4025.56		3974.94	4012.98	-0.16	3.4
	20	4295.63		4242.48	4282.97	-0.24	5.9

^a The rovibrational levels calculated using the DVR3D suite and the Bowman *et al* PES [116].

^b Experimental data [139, 113].

^c Obs-calc for VQZANO+ results corrected for the vibrational error.

^c Obs-calc for the Bowman *et al* [116] PES, corrected for the vibrational error.

^e The lowest rotational state for (01^{1e}0), taken as vibrational error.

Table 5.13: HCN Band Dipole Strengths (Debye)

(ν'_1, ν'_2, ν'_3)	$(\nu''_1, \nu''_2, \nu''_3)$	μ_{QZ}^a	ANO/ μ AQCC ^b	VQZANO+/ μ AQCC ^c	CASSCF ^d	AQCC ^e	Expt. ^f
(0,1 ¹ ,0)	(0,0,0)	0.1996(3)	0.2001	0.1981	0.27		0.189(1)
(0,2 ^{2f} ,0)	(0,1 ¹ ,0)	0.1996(4)					0.188(4)
(0,2 ^{2e} ,0)	(0,1 ¹ ,0)	0.1996(9)					0.189(4)
(0,2 ⁰ ,0)	(0,0,0)	0.0482(2)	0.04395[5]	0.04495[5]	0.048		0.0496(2)
(0,0,1)	(0,0,0)	0.0018(4)	0.0010[4]	6[4] $\times 10^{-4}$	0.0	0.0012	0.001362(4)
(1,0,0)	(0,1 ¹ ,0)	0.0238(2)	0.02262	0.239	0.02		0.0226(1)
(0,3 ^{1e} ,0)	(0,0,0)	0.00358(3)	0.000510	0.000171			0.003263(1)
(0,1 ¹ ,1)	(0,0,0)	0.00908(7)	0.00858	0.00853			0.00824(5)
(1,0,0)	(0,0,0)	0.0853(3)	0.073[2]	0.0726[4]	0.095	0.070	0.0831(17)
(1,1 ¹ ,0)	(0,0,0)	0.0098(2)	0.0096	0.0098	0.013		0.00986(11)
(1,0,1)	(0,0,0)	0.00436(2)	4[2] $\times 10^{-4}$	5.86[2] $\times 10^{-4}$	0.0024	0.0024	0.0055
(2,0,0)	(0,0,0)	0.008592(2)	0.00439[1]	0.00425[1]		0.005221	0.00881(12)
(3,0,0)	(0,0,0)	0.001138(1)	7.76[4] $\times 10^{-4}$	8.39[2] $\times 10^{-4}$		0.00111	0.00103

^a Calculated with DVR3D, using wave functions from VQZANO+ PES and the μ_{QZ} dipole surface. Transitions upto J=4 were used. Standard deviation in the last digit given in brackets.

^b Calculated with DVR3D, using wave functions from Bowman *et al* PES [116] and the dipole surface of Jakubetz and Lan [117]. Only J= 0 $\rightarrow$ 1 transitions were used. Difference between P and R branch line dipole strengths in the last digit given, where applicable, in square brackets.

^c Calculated with DVR3D, using wave functions from VQZANO+ PES and the dipole surface of Jakubetz and Lan [117]. Only J= 0 $\rightarrow$ 1 transitions were used. Difference between P and R branch line dipole strengths in the last digit given, where applicable, in square brackets.

^d *Ab initio* CASSCF and CCI calculations of Jørgensen *et al* [54], transformed from integrated band intensities to band dipoles.

^e *Ab initio* TZP AQCC dipole and surface calculations of Jakubetz and Lan [117], transformed from integrated band intensities to band dipoles.

^f Experimental data [83, 125, 128, 137, 114].

Table 5.14: HNC Fundamental Band Dipole Strengths (Debye).

(ν'_1, ν'_2, ν'_3)	$(\nu''_1, \nu''_2, \nu''_3)$	μ_{QZ}^a	ANO/ μ AQCC ^b	VQZANO+/ μ AQCC ^c	AQCC ^c	Expt. ^d
(0,1 ¹ ,0)	(0,0,0)	0.4627(5)	0.4961	0.4922		1.04(27)
(0,2 ⁰ ,0)	(0,0,0)	0.1037(5)	0.1043[6]	0.1032[6]		
(0,0,1)	(0,0,0)	0.1035(3)	0.1003[3]	0.1058[4]	0.10	0.076(17)
(1,0,0)	(0,0,0)	0.1509(4)	0.1575[4]	0.1550[2]	0.16	0.108(16)
(0,0,2)	(0,0,0)	0.01383(3)	0.01208[4]	0.01453[2]	0.013	

^a Calculated with DVR3D, using wave functions from VQZANO+ PES and the μ_{QZ} dipole surface. Transitions upto J=4 were used. Standard deviation in the last digit given in brackets.

^b Calculated with DVR3D, using wave functions from Bowman *et al* PES [116] and the dipole surface of Jakubetz and Lan [117]. Only J= 0 $\rightarrow$ 1 transitions were used. Difference between P and R branch line dipole strengths in the last digit given, where applicable, in square brackets.

^c Calculated with DVR3D, using wave functions from VQZANO+ PES and the dipole surface of Jakubetz and Lan [117]. Only J= 0 $\rightarrow$ 1 transitions were used. Difference between P and R branch line dipole strengths in the last digit given, where applicable, in square brackets.

^d *Ab initio* TZP AQCC dipole surface and calculations of Jakubetz and Lan [117], transformed from integrated band intensities to band dipoles.

^e Experimental data [140, 141].

Chapter 6

Room Temperature Spectra.

In this chapter I present *ab initio* room temperature (298K) spectra for HCN and HNC. Along with band centres and transition dipoles for the prominent features in the room temperature spectra. Line intensities are quoted for the HCN CN stretch fundamental band, which has unusual intensity structure, and also for the forbidden (02²0) bend overtone. Pure rotational $J = 1 \rightarrow 0$ transition dipoles in the ground and excited states of HCN/HNC are also presented.

At room temperature the internal energy of a gas is considerably lower than at stellar temperatures. Consequently we need only consider the lower lying rotational levels. This allowed the calculation of these room temperature spectra prior to the completion of the linelist. In fact the following spectra were computed using transitions up to only $J = 25$, see ref [172].

In section 6.1 we describe the computation of the linelist, in section 6.2 the spectra are presented and finally we conclude in section 6.3.

6.1 Calculation.

The partially completed linelist has been used to calculate room temperature (298 K) absorption spectra of HCN/HNC and also HNC as a separate molecule. The spectral calculations were limited to bands which have lines with absolute intensity above $4 \text{ cm}^{-1} \text{ mol}^{-1}$. Figures 6.1 and 6.2 show a spectral map of the HCN/HNC spectrum over the range 0 to 18000 cm^{-1} , the intensity of HNC bands at room temperature is less than the cut off intensity, so there are no HNC bands shown in this spectrum. The calculations were performed with the DVR3D suite of codes [122, 123] and the VQZANO+ PES and μQZ

DMS of this work, see chapter 4. Figure 6.3 shows the spectrum in the region of the HCN (40^0_0) stretching overtone.

To ease comparison with experiment and earlier *ab initio* work, the line transition dipole data was reduced to band transition dipoles for all the HCN bands shown in the spectrum and for other selected bands, see tables 6.1 and 6.2. For a given band this was done by dividing each line transition dipole by the square root of the appropriate Hönl–London and vibrational intensity factors to give the band dipole for that line, see section 3.2. The mean band dipole and the standard deviation were calculated using the band dipole calculated from each line. The standard deviation thus measures the reliability of using band dipoles and Hönl–London factors, it does not account for the systematic errors in the calculation.

For a band with unusual or perturbed structure it is more meaningful to compare line intensities directly than it is to compare fitted band dipoles and Herman-Wallis constants. For this reason two bands for which band transition dipoles are inappropriate are not included in the band dipole table. These bands are the HCN C-N fundamental (00^0_1) (see table 6.3) which has unusual R branch structure, see Maki *et al* [128], and the forbidden HCN bend overtone (02^2_0) (see table 6.4). For these bands we compare the calculated absolute lines intensities with experimental absolute line intensities.

Within the linelist the HCN and HNC transitions are mixed together with transitions involving the ‘delocalised’ states. To produce a room temperature HNC only spectrum it is necessary to separate the localised HNC transitions from the other transitions. Bowman *et al* [118] have suggested using the sign of the permanent dipole moment of a vibrational level to identify it as a HCN or HNC state. It is difficult to obtain absolute information from our calculated transition dipoles, so in this work HNC and HCN states are separated by comparing the transition dipole of a rovibrational state to the ground HCN state and to the ground HNC state. Localised HNC states will have a far greater transition dipole to the HNC ground state than to the HCN ground state. This allows the identification of localised HNC energy levels and transitions between them. Using this method only a handful of HCN states were mis-identified as HNC states, these tended to be HCN states with extremely low transition dipoles to the ground state, for example the HCN bending overtone (08^8_0) $\leftarrow$ (00^0_0) which is a strongly dipole forbidden transition. Transitions involving these few mis-identified states were removed by hand. It may also be possible to identify delocalised states using this method. The wave functions of delocalised states have

significant magnitude in both HCN and HNC potential wells and so should have similar transition dipole to the low lying localised states. However as a result of the problems discussed above this is a qualitative method and is not wholly reliable.

A fully *ab initio* partition function is presently being calculated by a collaborator, but at present despite my literature searches we have not found a partition function for HNC. This effects only calculation of absolute intensities for HNC and will not effect the spectra in which we give relative intensities or band transition dipoles.

Figure 6.5 shows a spectral map of HNC in absorption for 0 to 8000 cm^{-1} , figure 6.6 is the absorption spectrum in the region of the Q and R branch of the bending fundamental. Band transition dipoles for the prominent HNC bands are compared with existing experimental and theoretical values in tables 6.5 and 6.6.

Finally from the $J = 0 \rightarrow 1$ pure rotational transitions in the HCN and HNC ground and some HCN excited states, we give vibrationally averaged permanent dipoles and compare them with experiment and the *ab initio* vibrationally averaged dipole moments calculated by Bowman *et al* [118], see table 6.7.

The vibrationally averaged dipole moment of a given state is approximately equal to the $J = 0 \rightarrow 1$ pure rotational transitions from the following argument. The rotational transition dipole moment for a given vibrational level n is given by: $\langle nJ' | \underline{\mu} | nJ'' \rangle$. The vibrationally averaged dipole moment is the case where $J' = J'' = 0$ and can be approximately equated to the rotational transition dipole multiplied by the correct Hönl–London factor:

$$\langle n0 | \underline{\mu} | n0 \rangle \approx \langle nJ' | \underline{\mu} | nJ'' \rangle H_J \quad (6.1)$$

Furthermore $H_J = 1$ for the case where $J' = 1$ and $J'' = 0$. Therefore the $J = 1 \rightarrow 0$ pure rotational transition dipole is equal to the vibrationally averaged dipole moment within the approximations made when using Hönl–London factors.

6.2 Results and Discussion.

6.2.1 HCN Spectrum.

Overall for transitions involving the lower energy levels ($< 10000 \text{ cm}^{-1}$) the transition dipoles of our bands (see tables 6.1, 6.2) agree in most cases to within combined errors with experimental work and the *ab initio* work of Botschwina *et al* [131]. However for

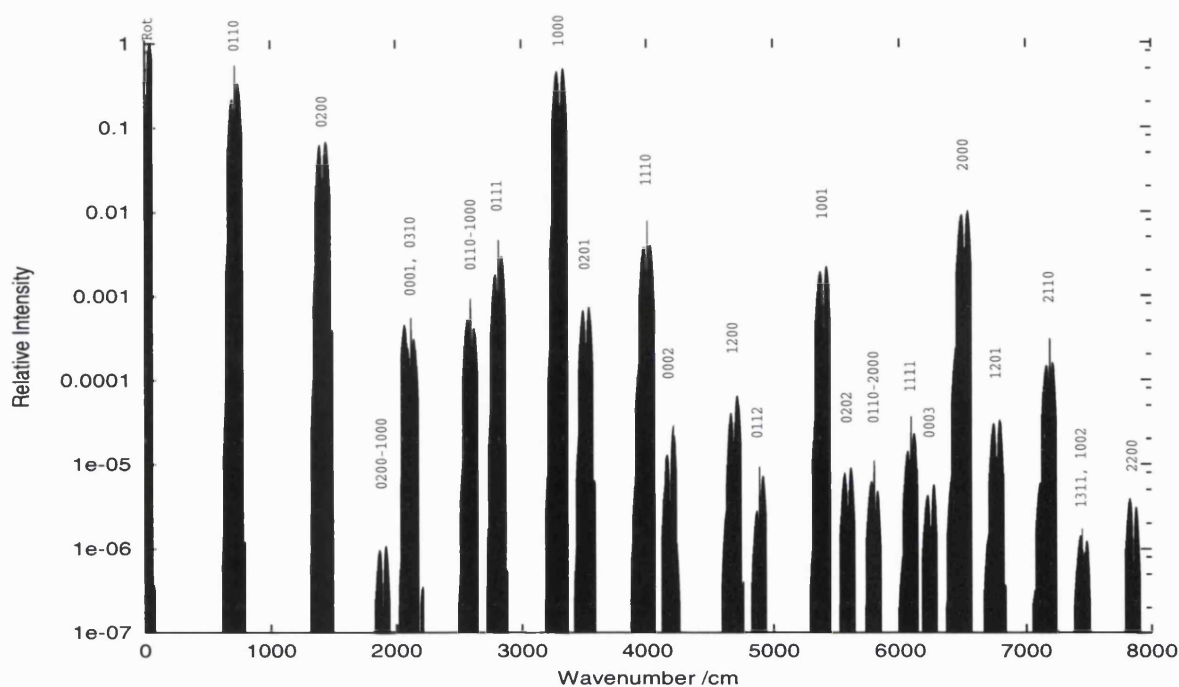


Figure 6.1: *Ab initio* spectral atlas for HCN in absorption, between 0 and 8000 cm^{-1} at 298 K. transitions are labeled $v'_1v'_2l'v'_3$ for transitions from the ground state and $v'_1v'_2l'v'_3-v''_1v''_2l''v''_3$ for transitions from an excited state.

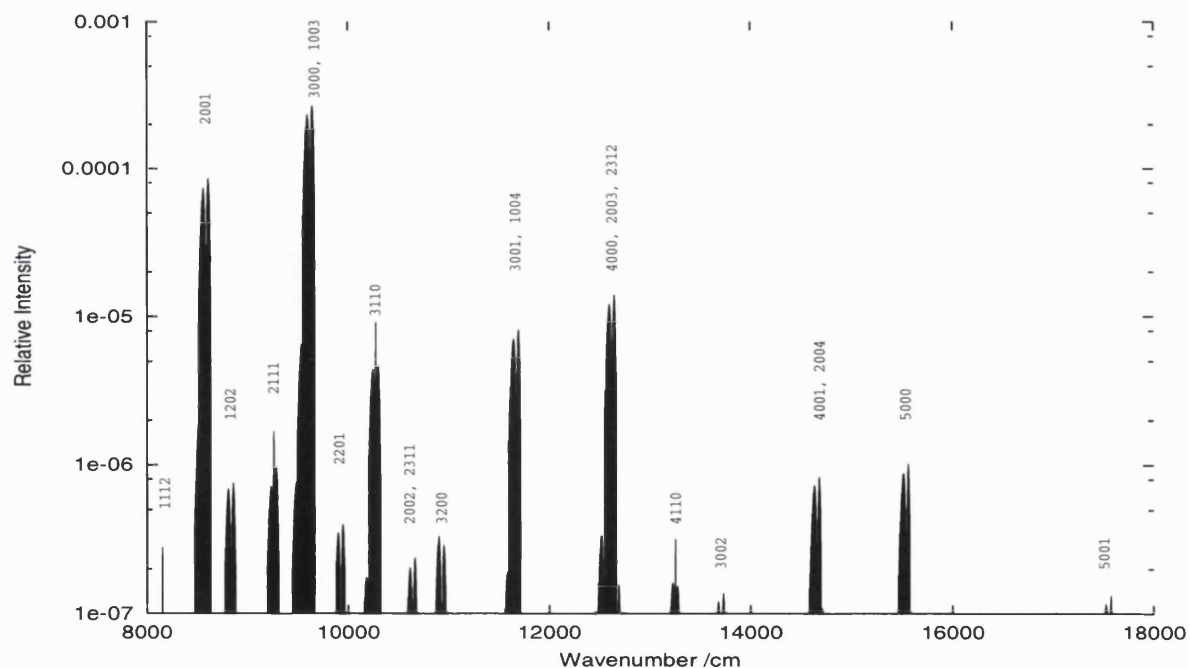


Figure 6.2: *Ab initio* spectral atlas for HCN in absorption, between 8000 and 18000 cm^{-1} at 298 K. transitions are labeled $v'_1v'_2l'v'_3$ for transitions from the ground state and $v'_1v'_2l'v'_3-v''_1v''_2l''v''_3$ for transitions from an excited state.

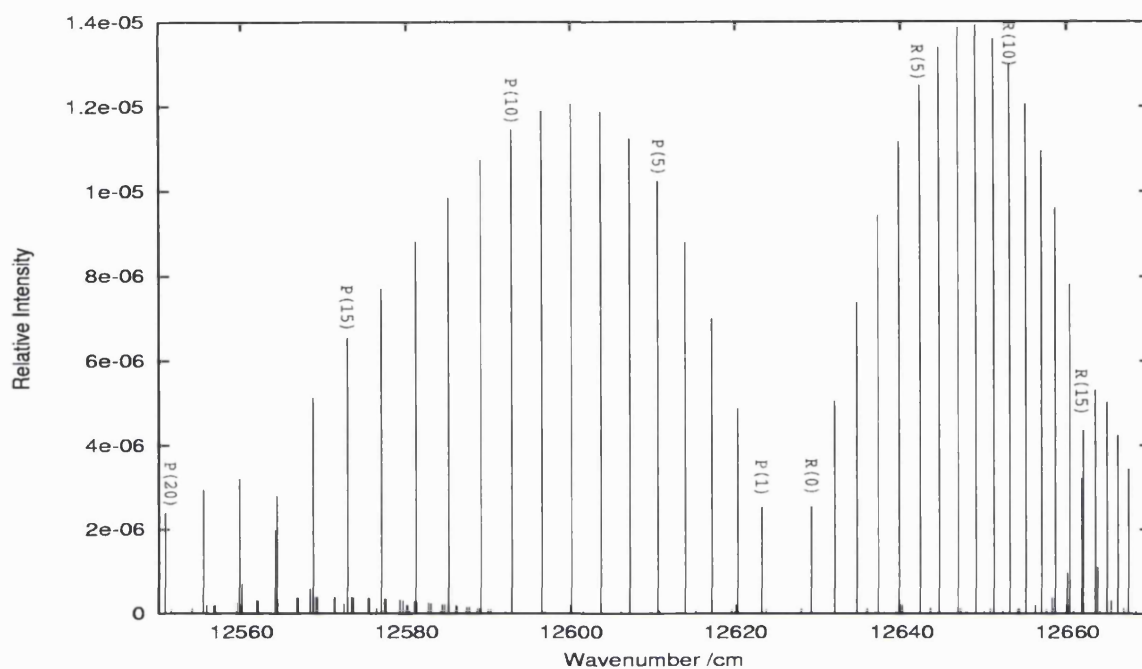


Figure 6.3: Absorption spectrum in the region of the HCN (40^0_0) overtone at 298K. The HCN (40^0_0) overtone shows a significant dip in intensity as a result of intensity borrowing in the region of the $J'' = 17$ P branch line and the $J'' = 15$ R branch line.

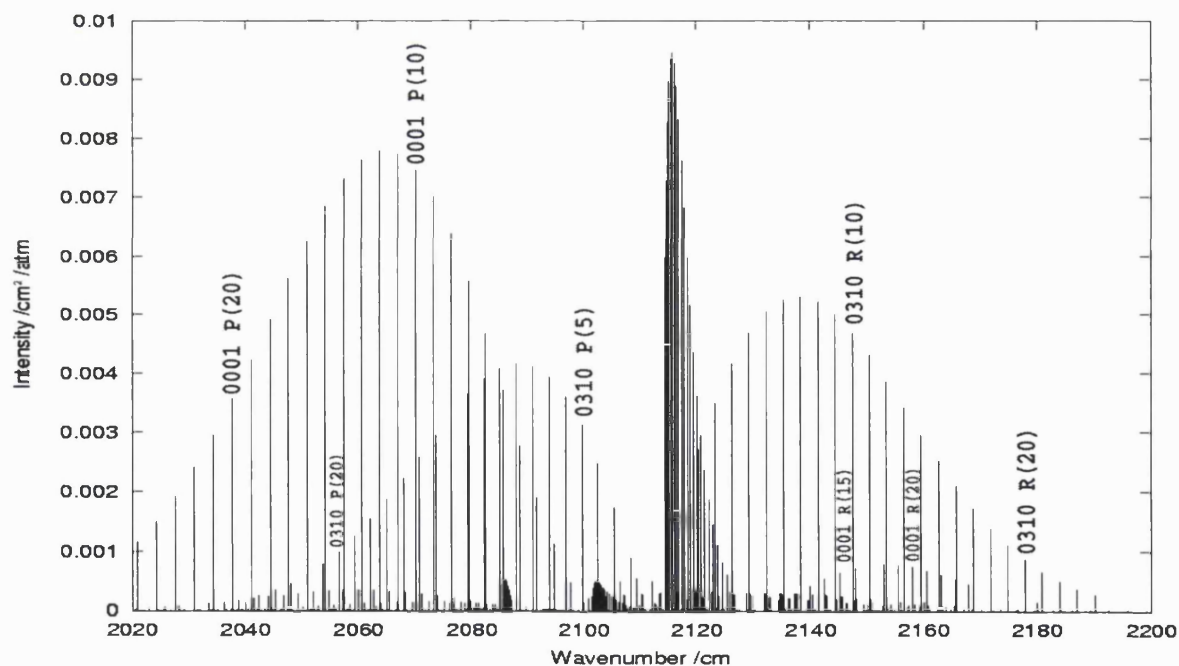


Figure 6.4: The *ab initio* HCN absorption spectrum in the region of the HCN (00^0_1) fundamental at 298 K. Some lines for the P and R branches of the (00^0_1) fundamental and the (03^1_0) bend overtone are labeled.

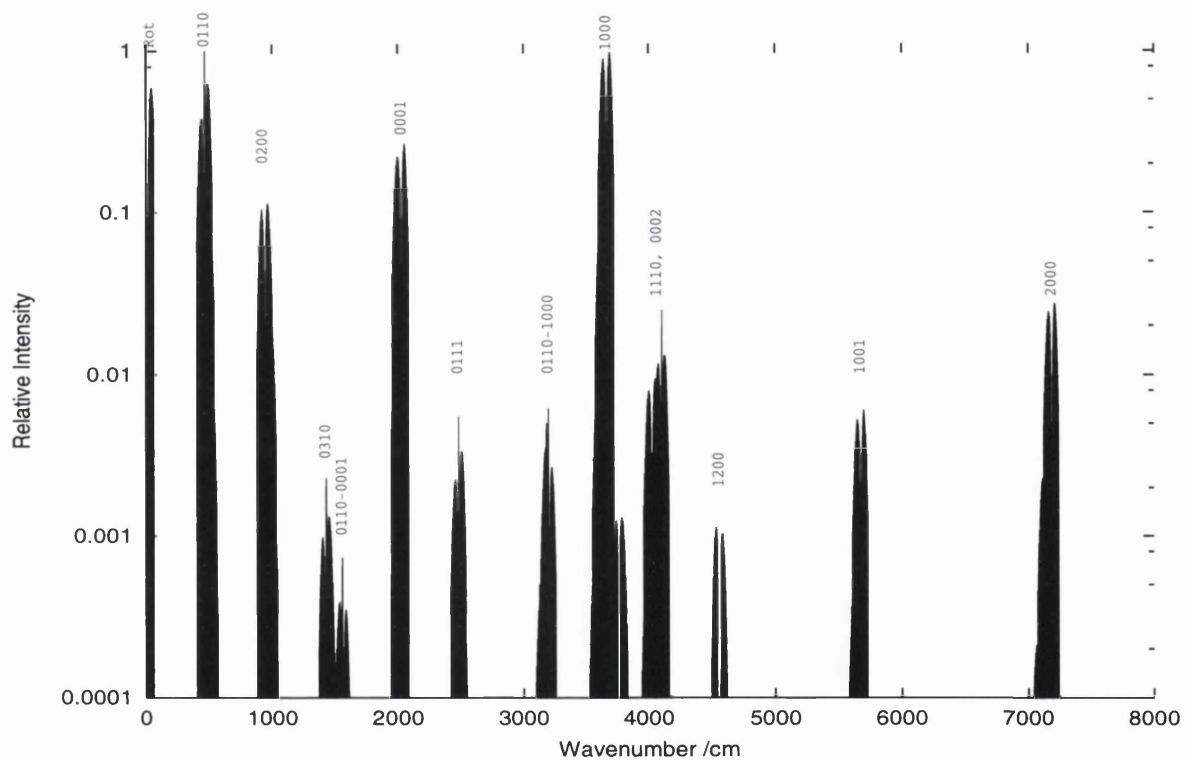


Figure 6.5: *Ab initio* spectral atlas for HNC in absorption, between 0 and 8000 cm^{-1} at 298 K. transitions are labeled $v'_1 v'_2 l' v'_3$ for transitions from the ground state and $v'_1 v'_2 l' v'_3 - v''_1 v''_2 l'' v''_3$ for transitions from an excited state.

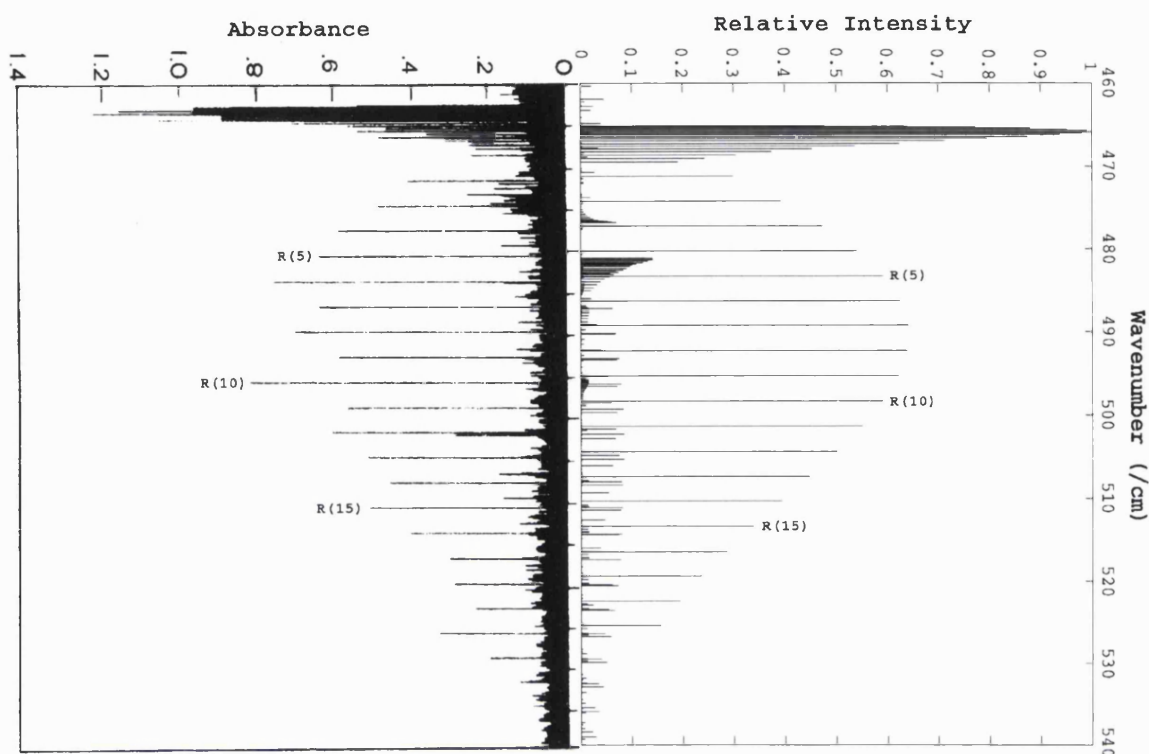


Figure 6.6: A comparison of *ab initio* and experimental [139] absorption spectra in the region of the Q and R branch of the HNC (01^1_0) fundamental at 298 K.

transitions involving the higher energy levels ($> 10000 \text{ cm}^{-1}$) there are more significant deviations from experiment with five band dipoles differing from experiment by a factor of two. These transitions are (20^0_3) , (31^1_0) , (41^1_0) , (20^0_4) and (40^0_2) . There appears to be something anomalous about the (31^1_0) measurement which is not reproduced by our calculations which predict that $(n1^1_0)$ should have $\mu \sim 10^{-(n+1)} \text{ D}$ and agree well with experiment and theory for $n = 1, 2, 4, 5$. The stretching combination bands (20^0_3) , (20^0_4) and (40^0_2) each lie within 40 cm^{-1} of a strong stretching combination band, these bands forming a pair of bands which interact, the band pairs being: (40^0_0) and (20^0_3) , (20^0_4) and (40^0_1) , (20^0_5) and (40^0_2) . The difference between the band centres of each band pair in our calculations tends to differ from experiment by about 10 cm^{-1} , this will serve to increase or decrease the interaction between the bands in each pair depending on whether the bands are closer together or further apart. The individual band intensities of these pairs of bands have not been reproduced accurately via fully *ab initio* techniques. Indeed Botschwina *et al* [131] who used a smaller 130 cGTO basis HCN stretching PES and 110 cGTO basis DMS, sidestepped the problem by calculating combined band intensities for each pair. To accurately reproduce experiment for these interacting bands, very accurate

wave functions are needed, as was shown by Botschwina [132] who reproduced experiment more accurately by using an empirical correction to his wavefunctions.

In astronomical applications a deviation of $> 10 \text{ cm}^{-1}$ on a strong band might have a significant effect on the opacity of a model atmosphere. If, for example, this error displaces a band into a region where there is little absorption it will stop energy escaping from the model atmosphere. This in turn will create an artificial warming effect within the atmosphere. The opposite of this, a cooling effect, is also possible. An error this large is detectable in the spectra of C-stars observed with the current generation of infrared space telescopes. It therefore might hinder the comparison of synthetic and observed C-star spectra. If these errors do prove to be a problem the frequencies of the lines in the linelist presented in chapter 7, may need correction. This could be accomplished by substituting experimentally determined energy levels and hence line frequencies, when and where available, for their *ab initio* counterparts. In such a linelist experimentally determined line frequencies are used in conjunction with *ab initio* line intensities.

Overall our calculations agree to a similar level of accuracy as the calculations of Botschwina *et al* [131] and agree more closely to experiment in the case of the (30^0_3) overtone from which the dipole from Botschwina deviates by a factor of two. It must be stressed that the calculations of Botschwina *et al* involve only 2 dimensional HCN stretching co-ordinates and use 2 dimensional potential and dipole functions only and give no information on bending excitations. Our band transition dipoles are significantly better than the AQCC calculations of Jakubetz and Lan [117] supporting our choice of dipole surface.

There are two bands in our spectrum which have not yet been experimentally identified and should be experimentally detectable, these are $(11^1_2) \leftarrow (00^0_0)$ and $(23^1_1) \leftarrow (00^0_0)$. There is an element of intensity borrowing present in some bands, one particular example is the $(40^0_0) \leftarrow (00^0_0)$ band, see fig 6.3. This band shows a significant dip in intensity as a result of intensity borrowing by the $(23^1_2) \leftarrow (00^0_0)$ band in the region of the R(15) and P(17) line. Intensity borrowing is not accounted for by Hönl–London factors, so our band intensities were calculated using lines from outside the regions in which intensity stealing was taking place. The errors on our band transition dipoles are a statistical measure of how well suited to fitting the intensity structure of a band Hönl–London factors are. For some bands, such as the $(04^2_e_0) \leftarrow (01^1_0)$ bend hot band, errors are as much as 20%. Hönl–London factor will not accurately reproduce the intensity structure of these bands.

Table 6.3 compares the experimental results of Maki *et al* [128] for the (00⁰1) band with our *ab initio* line intensities. The P branch *ab initio* line intensities are approximately 30% stronger than the experimental intensities. The *ab initio* R branch peak, reach minimum and peak again at $J'' = 2, 8$ and 18 respectively each of which are just above the experimental values at $J'' = 1, 7$ and 16 respectively. The intensities of the R branch lines beyond the minimum ($J'' > 11$) agree well with experiment. None-the-less for this band our calculations are in reasonable agreement with experiment and amount to the first fully *ab initio* reproduction of the intensity structure of this band. The spectrum in the region of the (00⁰1) fundamental is plotted in figure 6.4. The P branch of the (00⁰1) fundamental band and the P, Q and R branches of the (03¹0) overtone band are the major features in the spectrum. The unusually low intensity of the R branch of the (00⁰1) fundamental is clear in this figure.

Botschwina *et al* [133] using wavefunctions determined from the spectroscopically fitted HCN potential surface of Carter *et al* [136] and their own *ab initio* 110 cGTO/CCSD(T) dipole surface have calculated the band dipole for the (00⁰1) fundamental to within experimental error. The calculations of Botschwina *et al* described the unusual structure of this band for the first time and they determined a value of $A_1 = -0.188$ for the first order Herman-Wallis constant which agrees reasonably well with the experimentally determined value $A_1 = -0.1254$ of Maki *et al* [128]. Their value of A_1 , however, under predicts the position of the minimum in the R branch putting it at about $J'' = 4$ compared to the experimental value of $J'' = 7$ and our *ab initio* value at $J'' = 8$. This highlights the high level of sensitivity of the R branch structure to the wave functions and dipole surfaces used in the calculation.

The (02²0) bend overtone is forbidden by the normal dipole selection rules for a linear triatomic which are, for parallel transitions:

$$\Delta J = 0, \pm 1, \Delta l = 0 \quad (6.2)$$

with $\Delta J = 0$ not allowed if $l = 0$. For perpendicular transitions:

$$\Delta J = 0, \pm 1, \Delta l = \pm 1 \quad (6.3)$$

Some bending states with different orbital angular momentum (l) can become coupled by Coriolis interactions, resulting in l being poorly defined. In this event the selection rules on l are not rigidly obeyed. The (02²0) overtone intensities we have calculated are given in table 6.4, they compare well with the experimental intensities of Maki *et al* [137].

The P and R branch, except for the $J'' = 5$ line, agree to within 25% of experiment and the Q branch also agrees well, to within 30% of experiment. The calculated band centre at 1432.24 cm^{-1} agrees to within 8 cm^{-1} with the experimental value from Maki *et al* [138] of 1424.76 cm^{-1} .

The band centres are compared with experiment and the stretching vibrational band origins of Bowman *et al* [116], in table 6.2. Our calculated HCN band centres agree reasonably well with experiment, for transitions with frequency of less than 10000 cm^{-1} the mean deviation from experiment is 5 cm^{-1} , for transitions with frequency greater than 10000 cm^{-1} the mean deviation from experiment is 11 cm^{-1} . In general our stretching band centres are closer to experiment than those of Bowman *et al* [116]. A fuller discussion of band origins calculated with the VQZANO+ surface is given in chapter 4.

6.2.2 HNC spectrum.

Figure 6.5 is a spectral map of room temperature (298K) HNC in absorption, and figure 6.6 plots my spectrum against the experimental spectrum of Burkholder *et al* [139] in the region of the Q and R branch of the HNC bending fundamental. The dominant features of both the experimental and *ab initio* spectra in fig 6.6 are the Q and R branch of the bending fundamental, but also visible are the Q branches of the bending hot bands. The Q branch of the $(02^0_0) \leftarrow (01^1_0)$ band in the experimental spectrum can just be made out within the Q branch of the bending fundamental and the Q branch of the $(02^2_0) \leftarrow (01^1_0)$ is clearly visible. The Q branches of the $(02^0_0) \leftarrow (01^1_0)$ and $(02^2_0) \leftarrow (01^1_0)$ in the *ab initio* spectrum at 476.794 cm^{-1} and 481.117 cm^{-1} respectively are displaced from the experimental Q branches at 463.787 cm^{-1} and 473.471 cm^{-1} due to inaccuracy of the VQZANO+ potential surface. All the band transition dipoles and the band centres of the major features in the spectrum (fig. 6.5) are tabulated in tables 6.5 and 6.6. Although we get relatively good agreement with experiment, the situation for HNC is not as good as HCN. In turn the *ab initio* surfaces available for HCN/HNC are not as good as some other triatomics, for example water, so there is still work to be done on the *ab initio* surfaces of HCN/HNC.

Experimental data for band dipoles are only available for the HNC fundamentals [140, 141], the *ab initio* calculations of this work agree very well with both experimental and theoretical work for the stretching fundamentals. However for the bend fundamental our calculation is in agreement with the only other theoretical value [142], but disagrees

with experiment. The bending transition dipole was not directly measured by Nezu *et al* [140], but determined from the transition dipoles of the stretching fundamentals using the Herman-Wallis effect. As both theoretical values agree it is likely that the value of Nezu *et al* is in error, in fact Nezu *et al* [141] express doubts about the accuracy of their determination of the transition dipole of the bending fundamental. Beyond the fundamental bands theoretical intensity work has been done only on the stretching overtones [117, 131], our stretching overtones are in agreement with both theoretical works.

My calculated band centres and the *ab initio* energy levels of Bowman *et al* [116] for the CN stretching bands are of comparable accuracy, for the HN stretching bands our calculations are closer to experiment, see table 6.5. Maki and Mellau [143] estimated the band centre of the (03¹0) overtone from anharmonic vibration constants of HNC up to the quartic terms which were fitted to their experimental data with a standard deviation of 16 cm⁻¹. The large standard deviation of their fit implies that estimates of band centres from these constants will not be very accurate and as a result the large deviation from theory seen in Table 6.6 is to be expected. The stretching only HNC band centre calculations of Botschwina *et al* [131] are in good agreement with experiment. This is despite using a 133 cGTO basis which is smaller than the cc-pCVQZ basis (198 cGTO) used for part of the VQZANO+ PES [23]. However the HNC potential of Botschwina *et al* [131] considered stretching only co-ordinates. Experiment and the *ab initio* calculations of this work for the band centres of the HNC N-H stretch fundamental and overtone deviate by 12.5 and 18.0 cm⁻¹ respectively. It is likely that this deviation is caused by the cc-pCVQZ/aug-cc-pCVQZ basis not being large enough to accurately describe the electronic structure of the molecule at HNC geometries in the R co-ordinate.

6.2.3 Dipole Moments.

The $J = 1 \rightarrow 0$ pure rotational transition dipole calculated in this work is compared to experimental data and the *ab initio* vibrationally averaged dipole moments calculated by Bowman *et al* [118] in table 6.7. The HCN ground state and excited states for our dipole moment agree marginally less favorably with experiment than those of Bowman *et al*. However for the HNC ground state we agree significantly better with observation than Bowman *et al* [118], which deviates from experiment by -0.078 D and gives a value for the HNC ground state dipole that is lower than that of the HCN ground state dipole. Botschwina *et al* [133] used the empirical PES of Carter *et al* [136] and a 110 GTO *ab*

initio dipole moment surface for their calculations. Their results agree more closely with experiment than do the two fully *ab initio* calculations. Implying that the errors in the fully *ab initio* calculations are primarily due to the *ab initio* wavefunctions not being accurate enough.

Stanton [144] provided Bowman *et al* [118] with benchmark calculations, at the cc-pCVQZ/CCSD(T) level, of the dipole moment at the three critical points of the system. The dipole moment given by the μ QZ DMS of this work, see chapter 4, at the geometries of the critical points calculated at the cc-pCV5Z/CCSD(T) level by van Mourik *et al* [23] are given in table 6.8. The dipole moments from the μ QZ DMS are in good agreement with the calculations of Stanton [144] and the dipole moment from the DMS of Bowman *et al* [116].

6.3 Conclusion

Room temperature spectra, band centres and band transition dipoles of HCN and HNC have been calculated using the purely *ab initio* HCN/HNC linelist of this work. Features in the spectra, including the region of the HCN CN stretching fundamental and the HNC bending fundamental, match well the features of HCN and HNC spectra in published figures. I have plotted and assigned bands to a HCN spectral map in the range 0–18000 cm^{-1} and to a HNC spectral map in the range 0–8000 cm^{-1} .

In general our band centres agree more closely with experiment than do the *ab initio* energy levels of Bowman *et al* [116] calculated with their global *ab initio* PES. Our band transition dipoles for both HCN and HNC agree more closely with experiment than do those of the *ab initio* global DMS Jakubetz and Lan [117] and are of comparable accuracy to the stretching only CCSD(T) calculations of Botschwina *et al* [131]. We have also reproduced the unusual structure of the HCN CN stretch fundamental via fully *ab initio* techniques for the first time and have calculated the intensities of the forbidden Q branch of the HCN (02²0) overtone, which compare well with experiment.

Finally our HCN $J = 1 \rightarrow 0$ transition dipoles compare well with experiment and also with the vibrationally averaged dipole moments of Bowman *et al*.

Reported here are band transition dipoles for several HCN and many HNC bands for which no experimental or computationally determined band transition dipoles have previously been reported.

An important reason for using *ab initio* techniques for calculating rotation-vibration is

that these predictions are useful for spectral analysis. In particular the use of variational nuclear motion calculations and *ab initio* has provided means of assigning otherwise unanalysable spectra [145]. A key feature of this *ab initio* procedure, often not shown by methods which involve fitting to spectra, is that rotational progressions can be reliably extrapolated [146]. This means that once allowance is made for the overall band error, predictions can be very reliable. The present calculations, see Fig 6.6 for example, reproduce the rotational structure of the spectra accurately and will form a good starting point for further spectral analysis.

Table 6.1: A comparison of experimental and theoretical band centres and transition dipoles for the most prominent HCN bands at 298 K that have excitation in the bending mode, in cm^{-1} and Debye and standard deviation in the last digit given in brackets.

$v'_1 v'_2 l' v'_3$	$v''_1 v''_2 l'' v''_3$	Experiment ^a		This Work ^b	
		ν_0	μ	ν_0	μ
0 4 2 0	0 3 1 0	674.414		668.30	0.184(3)
0 3 1e 0	0 2 2 0	686.921	0.188(1)	682.13	0.175(13)
0 3 1f 0	0 2 2 0	686.921	0.189(1)	682.22	0.202(11)
0 4 0 0	0 3 1 0	689.509	0.185(3)	687.10	0.196(26)
0 2 0 0	0 1 1 0	699.434	0.183(5)	699.03	0.199(17)
0 3 1 0	0 2 0 0	702.037	0.190(2)	699.50	0.197(8)
0 4 2e 0	0 3 1 0	704.725	0.196(5)	702.91	0.187(31)
0 4 2f 0	0 3 1 0	704.725	0.188(7)	703.00	0.196(4)
0 1 1 0	0 0 0 0	711.980	0.189(1)	715.93	0.200(1)
0 2 2e 0	0 1 1 0	714.550	0.189(4)	716.30	0.196(17)
0 2 2f 0	0 1 1 0	714.550	0.188(4)	716.35	0.200(2)
0 3 3e 0	0 2 2 0	717.231	0.196(1)	716.87	0.198(5)
0 3 3f 0	0 2 2 0	717.231	0.197(1)	716.87	0.198(6)
0 4 4e 0	0 3 3 0	720.021		718.22	0.198(5)
0 4 4f 0	0 3 3 0	720.021	0.201(5)	718.22	0.198(5)
0 4 2e 0	0 2 2 0	1391.65	0.0486(2)	1385.12	0.0470(14)

Table 6.1: continued.

$v'_1 v'_2 l' v'_3$	$v''_1 v''_2 l'' v''_3$	Experiment ^a		This Work ^b	
		ν_0	μ	ν_0	μ
0 4 2f 0	0 2 2 0	1391.65	0.0488(2)	1385.12	0.0475(12)
0 4 0 0	0 2 0 0	1391.56	0.0489(2)	1386.55	0.0470(10)
0 3 1e 0	0 1 1 0	1401.47	0.0471(2)	1398.43	0.0496(35)
0 3 1f 0	0 1 1 0	1401.47	0.0475(4)	1398.57	0.0463(32)
0 2 0 0	0 0 0 0	1411.41	0.0496(2)	1414.92	0.0479(11)
1 0 0 0	0 2 0 0	1900.06		1892.83	0.00498(7)
0 4 0 0	0 1 1 0	2090.98	0.00320(1)	2085.62	0.00369(50)
0 4 2e 0	0 1 1 0	2106.20	0.00330(2)	2101.43	0.00342(65)
0 4 2f 0	0 1 1 0	2106.20	0.00327(1)	2101.48	0.00357(14)
0 3 1 0	0 0 0 0	2113.45	0.003263(1)	2114.46	0.00359(15)
1 2 0 0	0 3 1 0	2570.86	0.0228(1)	2571.81	0.0236(14)
1 1 1e 0	0 2 2 0	2577.63	0.0232(1)	2571.98	0.0229(17)
1 1 1f 0	0 2 2 0	2577.63	0.0232(1)	2572.03	0.0245(15)
1 1 1 0	0 2 0 0	2592.75	0.0226(1)	2589.31	0.0239(24)
1 0 0 0	0 1 1 0	2599.50	0.0226(1)	2591.75	0.0238(10)
0 1 1 1	0 0 0 0	2807.06	0.00824(5)	2813.98	0.00906(36)
0 2 0 1	0 0 0 0	3502.12		3510.99	0.00313(6)
1 1 1 0	0 0 0 0	4005.63	0.00986(11)	4004.27	0.00986(94)
1 3 1e 0	0 1 1 0	4654.89	0.000784(3)	4650.21	0.000785(110)
1 3 1f 0	0 1 1 0	4654.89	0.000786(4)	4650.34	0.000781(80)
1 2 0 0	0 0 0 0	4684.31	0.000795(5)	4686.28	0.000735(93)
0 1 1 2	0 0 0 0	4879.73		4891.88	0.000310(51)
0 2 0 2	0 0 0 0	5571.89		5586.50	0.000272(3)
2 0 0 0	0 1 1 0	5806.15	0.00137(1) ^c	5797.45	0.00172(8)
1 1 1 1	0 0 0 0	6084.80	0.00052(4) ^c	6088.56	0.000545(19)
2 2 0 0	0 2 0 0	6441.54	0.00892(14)	6440.92	0.00789(1)
2 1 1e 0	0 1 1 0	6480.78	0.00889(4)	6474.62	0.00835(22)
2 1 1f 0	0 1 1 0	6480.78	0.00901(4)	6474.71	0.00826(6)
1 2 0 1	0 0 0 0	6761.33		6768.51	0.000479(7)

Table 6.1: continued.

$v'_1 v'_2 l' v'_3$	$v''_1 v''_2 l'' v''_3$	Experiment ^a		This Work ^b	
		ν_0	μ	ν_0	μ
2 1 1 0	0 0 0 0	7194.22		7190.60	0.00146(12)
1 3 1 1	0 0 0 0	7440.48		7445.62	0.000107(8)
2 2 0 0	0 0 0 0	7853.51		7855.83	0.000150(20)
1 1 1 2	0 0 0 0			8182.18	$4.14(6) \times 10^{-5}$
2 1 1 1	0 1 1 0	8544.07	0.00071(5) ^c	8543.75	0.000625(4)
1 2 0 2	0 0 0 0	8816.00		8830.27	$6.35(10) \times 10^{-5}$
2 1 1 1	0 0 0 0	9257.53	$8.2(6) \times 10^{-5}$ ^c	9259.64	$9.48(19) \times 10^{-5}$
3 1 1 0	0 1 1 0	9568.35	0.0010(4) ^c	9560.81	0.001082(9)
2 2 0 1	0 0 0 0	9914.40	$5.5(2) \times 10^{-5}$ ^c	9922.92	$4.31(2) \times 10^{-5}$
3 1 1 0	0 0 0 0	10281.8	$3.2(2) \times 10^{-5}$ ^c	10276.7	0.000210(19)
2 3 1 1	0 0 0 0			10580.5	$1.43(15) \times 10^{-5}$
3 2 0 0	0 0 0 0			10925.2	$3.78(28) \times 10^{-5}$
4 1 1 0	0 1 1 0	12557.3	0.00023(3) ^c	12548.1	0.000218(5)
2 3 1 2	0 0 0 0			12624.3	$1.55(1) \times 10^{-6}$
4 1 1 0	0 0 0 0	13270.8	$1.4(4) \times 10^{-5}$ ^c	13264.1	$3.47(42) \times 10^{-5}$
5 1 1 0	0 1 1 0	15452.1	$6.6(5) \times 10^{-5}$ ^c	15441.0	$5.32(6) \times 10^{-5}$
5 1 1 0	0 0 0 0	16165.6	$3.4(3) \times 10^{-6}$ ^c	16156.9	$6.67(115) \times 10^{-6}$ ^d

^a Experimental data, band centres taken from refs [138, 147, 129, 148, 149], transition dipoles from Maki *et al* [125] and from Smith *et al* [126, 129] where marked.

^b The *ab initio* calculations of this work, using the VQZANO+ PES and the μ QZ DMS of this work.

^c Experimental measurements of Smith *et al* [126, 129].

^d This band is involved in intensity stealing.

Table 6.2: A comparison of experimental and theoretical stretching band centres and transition dipoles for some of the most prominent HCN stretching bands at 298 K, in cm^{-1} and Debye ($\times 10^{-3}$), with standard deviation in the last digit given in brackets.

$v'_1 v'_2 l' v'_3$	$v''_1 v''_2 l'' v''_3$	Experiment ^a		This Work ^b		Earlier <i>ab initio</i> Work		
		ν_0	μ	ν_0	μ	ANO ^c ν_0	μ_{GTO} ^d	μ_{AQCC} ^e
1 0 0 0	0 0 0 0	3311.48	83.1(17)	3307.75	85.3(16)	3334.1	83.4	0.0703
0 0 0 2	0 0 0 0	4173.07		4181.45	0.466(52) ^h	4161.5	0.130	0.773
1 0 0 1	0 0 0 0	5393.70		5394.43	4.37(2)	5399.4	4.63	2.41
0 0 0 3	0 0 0 0	6228.60	0.12(2) ^f	6242.42	0.198(12)	6211.4	0.117	0.247
2 0 0 1	0 0 0 1	6488.74	8.7(3)	6484.16	8.49(3)			
2 0 0 0	0 0 0 0	6519.61	8.81(12)	6513.50	8.60(4)	6553.2	8.78	5.22
1 0 0 2	0 0 0 0	7455.42	0.11(1) ^f	7461.58	0.0959(91)	7445.7	0.0974	0.245
2 0 0 1	0 0 0 0	8585.58	0.68(1) ^f	8584.59	0.677(4)	8595.9	0.785	0.468
1 0 0 3	0 0 0 0	9496.44	0.066(3) ^f	9508.91	0.0648(8)	9474.5	0.0771	0.0796
3 0 0 0	0 0 0 0	9627.09	1.03(2) ^f	9619.20	1.138(6)	9668.3	1.12	1.11
2 0 0 2	0 0 0 0	10631.4	0.050(2) ^f	10636.8	0.0320(4)	10623.7	0.0614	0.0229
1 0 0 4	0 0 0 0	11516.6		11536.1	0.0114(7)	11487.4		
3 0 0 1	0 0 0 0	11674.5	0.185(4) ^f	11672.2	0.179(5)	11686.9	0.202	0.283

Table 6.2: continued.

$v'_1 v'_2 l' v'_3$	$v''_1 v''_2 l'' v''_3$	Experiment ^a		This Work ^b		Earlier <i>ab initio</i> Work		
		ν_0	μ	ν_0	μ	ANO ^c ν_0	μ_{GTO} ^d	μ_{AQCC} ^e
4 0 0 0	0 0 0 0	12635.9	0.222(7) ^f	12626.2	0.225(2) ^h	12686.1		
2 0 0 3	0 0 0 0	12658.0	0.053(4) ^f	12669.9	0.0239(5)	12638.6		
3 0 0 2	0 0 0 0	13702.2	0.029(2) ^f	13708.5	0.0216(1)	13695.5	0333	0.0499
2 0 0 4	0 0 0 0	14653.7	0.048(2) ^f	14685.0	0.0187(6)	14642.8		
4 0 0 1	0 0 0 0	14670.5	0.051(2) ^f	14656.9	0.0513(3)	14683.9		
5 0 0 0	0 0 0 0	15551.9	0.067(8) ^f	15539.3	0.0550(5)	15604.1	0.0671	0.165
3 0 0 3	0 0 0 0	15710.5	0.0036(4) ^f	15721.7	0.00487(3) ^h	15700.3	0.00730	0.00196
2 0 0 5	0 0 0 0	16640.3	0.0098(6) ^f	16660.7	0.00793(17)	16634.5		
4 0 0 2	0 0 0 0	16674.2	0.0202(8) ^f	16685.0	0.00786(20)	16683.6		
5 0 0 1	0 0 0 0	17550.4	0.0282 ^g	17551.0	0.0154(58) ^h	17574.4	0.0286	0.0755

^a Experimental data, band centres taken from refs [138, 147, 129, 148, 149], transition dipoles from Maki *et al* [125] and others where where marked.

^b The *ab initio* calculations of this work, using the VQZANO+ PES and the μ QZ DMS of this work.

^c The *ab initio* ANO/CCSD(T) vibrational energy level calculations of Bowman *et al* [116].

^d The *ab initio* 110 cGTO stretch only HCN DMS and calculations of Botschwina *et al* [131], Botschwina *et al* also calculated a combined intensities for three pairs of strong stretching bands: (40⁰0) and (20⁰3), (20⁰4) and (40⁰1), (20⁰5) and (40⁰2), see text.

^e The *ab initio* TZP AQCC semi-global DMS and calculations of Jakubetz and Lan [117], using the Bowman *et al* [116] potential surface.

^f Measurements of Smith *et al* [126, 129].

^g Measurement from Romanini and Lehmann [130].

^h These bands are involved in intensity stealing.

Table 6.3: A comparison of experimental and theoretical line intensities ($\text{cm}^{-2}\text{atm}^{-1} \times 10^{-3}$) for the HCN (00^01) fundamental band.

P Branch		J''	R Branch	
Expt ^a	This work		Expt ^a	This work
		0	0.193	0.323
0.337	0.487	1	0.300	0.497
0.839	1.14	2	0.295	0.541
1.36	1.92	3	0.236	0.497
2.03	2.81	4	0.171	0.385
2.87	3.75	5	0.0725	0.256
	4.71	6	0.0161	0.133
4.23	5.61	7		0.0445
4.97	6.44	8	0.0297	0.00249
5.55	7.08	9	0.124	0.0124
5.86	7.53	10	0.222	0.0705
6.11	7.80	11	0.358	0.167
6.09	7.85	12	0.506	0.288
6.00	7.70	13	0.670	0.420
5.84	7.37	14	0.796	0.544
5.46	6.91	15	0.910	0.651
5.08	6.31	16	1.00	0.730
4.66	5.67	17		0.778
4.06	4.97	18	0.988	0.792
3.51	4.26	19	0.967	0.778
2.97	3.60	20	0.895	0.736

^a Experimental measurements of Maki *et al* [128].

Table 6.4: A comparison of experimental and theoretical line intensities ($\text{cm}^{-2}\text{atm}^{-1} \times 10^{-3}$, standard deviation given in the last digit) for the HCN (02²0) forbidden overtone band.

J''	P Branch		R Branch		Q Branch	
	Expt. ^a	This work	Expt. ^a	This work	Expt. ^a	This work
2				0.000251		0.00606
3		0.00606		0.00601		0.0203
4		0.0104		0.0330		0.0442
5	0.022(8)	0.150	0.149(5)	0.106	0.061(3)	0.0785
6	0.481(8)	0.343		0.253		0.121
7	0.834(9)	0.663	0.80(2)	0.507	0.201(7)	0.171
8	1.357(21)	1.14	1.392(18)	0.890	0.252(6)	0.225
9	2.246(28)	1.77		1.41	0.291(5)	0.276
10	3.264(24)	2.56	2.899(37)	2.08	0.354(6)	0.326
11	4.445(25)	3.48	4.073(26)	2.82	0.406(6)	0.365
12	5.673(36)	4.48	5.352(25)	3.68	0.469(5)	0.397
13	7.097(36)	5.47	6.337(28)	4.52	0.455(6)	0.415
14	8.251(36)	6.41	7.447(37)	5.29	0.470(5)	0.422
15	9.141(46)	7.20	8.378(49)	5.96	0.439(7)	0.417
16	10.200(48)	7.82	8.895(47)	6.46		0.400
17	10.579(47)	8.19	9.357(52)	6.76	0.405(5)	0.375
18	10.645(79)	8.30	9.478(40)	6.83	0.390(5)	0.343
19	10.492(50)	8.17		6.70	0.346(5)	0.305
20		7.80	8.577(41)	6.32		0.266

^a The experimental measurements of Maki *et al* [137].

Table 6.5: A comparison of experimental and theoretical band centres (cm^{-1}) and transition dipoles (Debye, with standard deviation given in the last digit in brackets) for HNC fundamentals and some stretching overtones which are the prominent features of the spectrum at 298 K.

$v'_1 v'_2 l' v'_3$	Experiment ^a		This Work ^b		aug-cc-pVTZ ^c		Other Theory		
	ν_0	μ	ν_0	μ	ν_0	μ	ν_0^d	μ^e	μ^f
0 1 1 0	462.722	[1.04(27)] ^h	465.190	0.463(3)					0.490
0 0 0 1	2023.86	0.108(16)	2024.94	0.104(2)	2023.9	0.106	2024.6	0.103	0.102
1 0 0 0	3652.66	0.156(23)	3665.12	0.151(2)	3652.7	0.157	3599.1	0.157	0.164
0 0 0 2	4026.40 ^g		4029.20	0.0138(3)	4026.4	0.0136	4024.4	0.0126	
1 0 0 1	5664.85 ^g		5676.51	0.00943(2)	5664.1	0.00999	5628.7	0.00985	
2 0 0 0	7171.40 ^g		7189.53	0.0179(1)	7172.1	0.0163	7116.7	0.0134	

^a Experimental data, band centres from Maki and Mellau [143] and Northrup *et al* [150] and band transition dipoles from Nezu *et al* [140, 141].

^b The *ab initio* calculations of this work, using the VQZANO+ PES and the μ QZ DMS of this work.

^c The *ab initio* stretch only cc-pVQZ/CCSD(T) potential and aug-cc-pVTZ/CCSD(T) dipole surface calculations of Botschwina *et al* [131].

^d The *ab initio* ANO/CCSD(T) vibrational energy level calculations of Bowman *et al* [116], quoted here are stretching levels only, see text.

^e The *ab initio* TZP AQCC calculations of Jakubetz and Lan [117], using the Bowman *et al* [116] potential surface.

^f The TZ2P/CCSD(T) calculations of Lee and Rendell [142].

^g These transitions have not been directly measured, but have been inferred from other transitions.

^h The transition dipole of the bending fundamental was estimated from the stretching fundamental transition dipoles using Herman-Walis effect by Nezu *et al* [140], see text.

Table 6.6: A comparison of experimental and theoretical band centres (cm^{-1}) and transition dipoles (Debye, with standard deviation give to the last digit in brackets) of HNC hot bands and overtones which involve a degree of bending mode excitation and are prominent features in the spectrum at 298 K.

$v'_1 v'_2 l' v'_3$	$v''_1 v''_2 l'' v''_3$	Experiment ^a	This work	
		ν_0	ν_0	μ
0 2 0 0	0 1 1 0	463.787	476.794	0.466(154)
0 2 2 0	0 1 1 0	473.471	481.117	0.424(188)
0 2 0 0	0 0 0 0	926.507 ^b	941.910	0.0976(67)
0 3 1 0	0 0 0 0	[1400.51] ^c	1428.85	0.0673(77)
0 0 0 1	0 1 1 0		1559.69	0.0199(1)
0 1 1 1	0 1 1 0	2015.76	2017.54	0.103(16)
0 1 1 1	0 0 0 0	2478.48 ^b	2482.67	0.0141(1)
1 0 0 0	0 1 1 0		3199.88	0.0407(16)
1 1 1 0	0 1 1 0	3630.19	3640.77	0.146(5)
1 1 1 0	0 0 0 0	4092.91 ^b	4105.90	0.0227(14)
1 2 0 0	0 0 0 0	4534.45 ^b	4558.15	0.00455(42)

^a Experimental band centres from Maki and Mellau [143] and Northrup *et al* [150].

^b These transitions have not been directly measured, but have been inferred from other transitions.

^c This band centre was estimated by Maki and Mellau [143] from anharmonic vibration constants of HNC up to the quartic terms, see text.

Table 6.7: A comparison of experimental and theoretical vibrationally averaged dipole moments of $J = 0$ low lying HCN states and the HNC ground state.

(v_1, v_2, v_3)	Expt.	aug-cc-pCVTZ ^a	cc-pCVQZ ^b	110 cGTO ^c
(0,0,0)	2.985 ^d	2.9752	2.9641	2.9800
(0,2,0)	2.899 ^d	2.8793	2.8776	2.8935
(0,0,1)	2.981 ^d	2.9698	2.9599	2.9753
(1,0,0)	3.017 ^d	3.0054	2.9961	3.0116
(0,0,0) ^f	3.05 ^e	2.9721	3.0320	—

^a Dipole moment calculations of Bowman *et al* [118] with aug-cc-pCVTZ/CCSD(T) DMS.

^b This work, $J = 0 \rightarrow 1$ rotational transition dipole using cc-pCVQZ/CCSD(T) DMS.

^c Dipole moment calculations of Botschwina *et al* [133] with HCN-only 110 cGTO/CCSD(T) DMS.

^d Deleon and Muentner [22].

^e Blackman *et al* [151].

^f HNC ground state.

Table 6.8: A comparison of *ab initio* dipole moments (Debye) at the three critical points.

	aug-cc-pCVTZ DMS ^a	cc-pCVQZ DMS ^b	Optimised cc-pCVQZ ^c
HCN	2.999	2.993	2.994
TS ^d	1.171	1.181	1.178
HNC	−3.087	−3.121	−3.094

^a Dipole moments from the aug-cc-pCVTZ/CCSD(T) DMS of Bowman *et al* [118] at the co-ordinates of the critical points calculated by Stanton [144] at the cc-pCVQZ/CCSD(T) level.

^b The Dipole moments from the μ QZ DMS of this work at the co-ordinates of the critical points calculated at the cc-pCV5Z/CCSD(T) level.

^c Dipole moment at the critical points calculated by Stanton [144] at the cc-pCVQZ level.

^d The transition state of [H,C,N].

Chapter 7

The Full Linelist and Opacity Function.

In this chapter I give an overview of the calculation and the problems encountered during the duration of the calculation. I also give final results in the form of some high temperature spectra and an opacity function.

7.1 Optimising the Size of the Line-list.

The duration of the calculation is heavily dependent upon the maximum energy and the highest rotational levels to be calculated. The maximum energy and rotational level to be calculated in turn are determined by the astronomical requirements. The linelist must contain all rovibrational energy levels that are significantly populated at stellar temperatures (1500 to 3000 K). It is desirable to extend the linelist to vibrational energy levels to as high an energy as possible. The maximum value of J to be calculated can be estimated by considering the thermal distribution of rotational levels. In order to give a good representation of a band the maximum rotational level in the linelist must have a thermal population that is a fraction of the population of the most populated rotational level.

The peak of the statistical population of rotational levels at thermodynamic equilibrium can be estimated from equation 3.7. Using a value $B = 1.435 \text{ cm}^{-1}$ and a temperature of 3000 K. The most populated level is $J = 26$ clearly the calculation must proceed significantly beyond $J = 26$.

The linelist must include all bands that have been observed in the atmospheres of

C-stars and also their hot bands. Querci and Querci [46] claimed to detect the (40^0_0) band. However, using a new linelist based on experimental data Jørgensen [60] disputed that any bands beyond $1.5 \mu\text{m}$ could be observed in C-star atmospheres. For the sake of safety if we assume that the claim of Querci and Querci is correct, the energy of the $J=0$ (40^0_0) level is $\sim 12\,500 \text{ cm}^{-1}$. According to the Boltzmann equation at 3000 K, levels with energies of $\sim 5500 \text{ cm}^{-1}$ have $\sim 10\%$ the population of the ground state. Adding these two energies together we arrive at a minimum, maximum energy for the linelist of $18\,000 \text{ cm}^{-1}$. This maximum energy will allow the determination of opacity from all bands and their hot bands longwards of $0.8 \mu\text{m}$.

Test runs were performed for $J = 22$ and $J = 23$ to estimate run time. For $E_{max} = 18000 \text{ cm}^{-1}$ ROTLEV3 requires approximately 5 days per J . DIPOLE3B must be run a total of $3J_{max} - 1$ times at an estimated average 1.5 days per run. This would allow a calculation of up to $J = 40$, requiring an estimated time of 378 days. Fortunately the Miracle O2000 is sufficiently large to allow the simultaneous execution of ROTLEV3 and DIPOLE3B. As a result we will be calculating the linelist up to $E_{max} = 18000 \text{ cm}^{-1}$.

7.2 The Calculation of the Linelist.

The calculation of the HCN/HNC linelist started on 8th December 2000 and at present it has been running for over a year. All the calculations were performed on the HiPerSPACE [174] SGI O2000 24 processor computer, named Miracle, at UCL. The linelist was calculated using the DVR3D suite of codes [122, 123] with the new *ab initio* VQZANO+ PES and $\mu\text{QZ DMS}$ (see chapter 4).

7.2.1 Input Parameters.

The input parameters for DVR3DRJZ and ROTLEV3 were optimised as discussed in chapter 5. The parameters of these calculations are given in table 5.6 in the column marked final values. The one parameter that has been omitted from table 5.6 is NEVAL, the number of energy levels calculated by ROTLEV3. It was decided that the linelist would be truncated at $18\,000 \text{ cm}^{-1}$. Figure 7.1 shows the number of energy levels for the e and f states at a given J , divided by $2J + 1$, with energy less than $18\,000 \text{ cm}^{-1}$. Each of the rovibrational states in figure 7.1 is $(2J + 1)$ fold degenerate, consequently there are $(2J + 1)NEVAL$ states. So a curve showing number of energy levels verses J , does not peak in this region, but the total number of rovibrational states continues to increase.

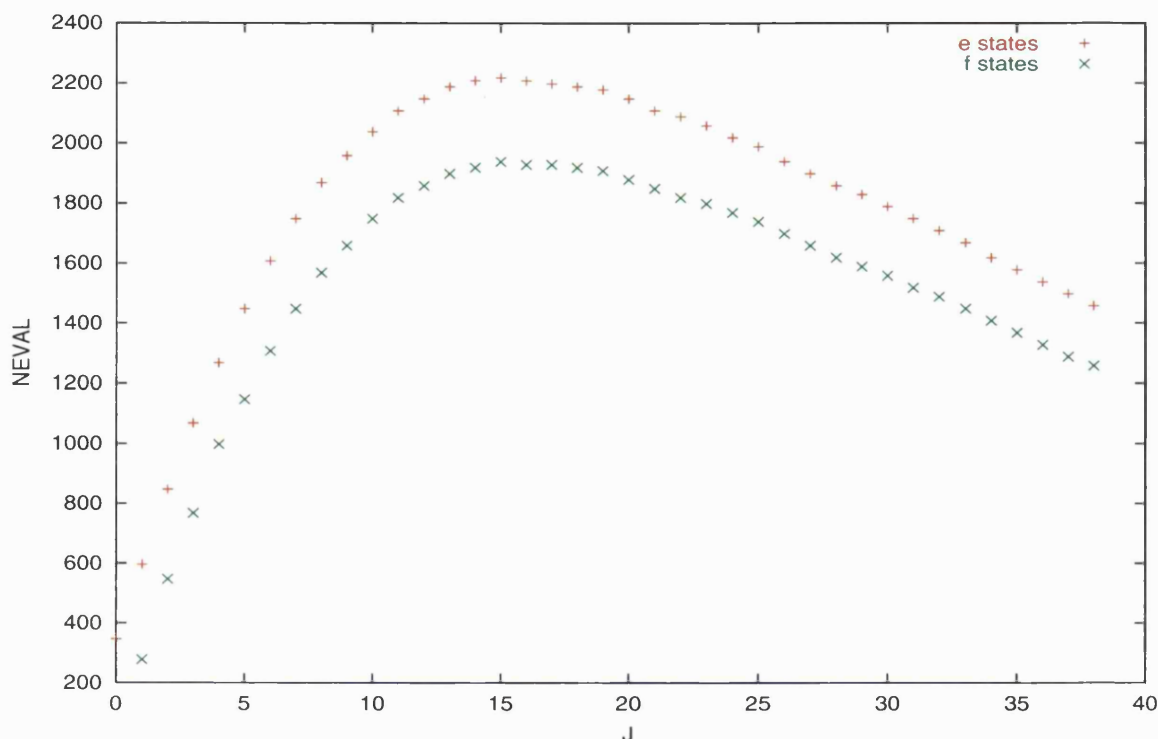


Figure 7.1: The number of rovibrational states divided by rotational degeneracy (NEVAL) with energy less than $18\,000\text{ cm}^{-1}$, to the nearest 10, as a function of J .

However only one of the rotationally degenerate states need be calculated, as long as the $2J + 1$ factor is kept in mind.

It is clear that NEVAL can be estimated for a given J, p from the preceding values of NEVAL. The reason for the shape of the curves in figure 7.1 is a consequence of two factors. Firstly, states with $l \leq J$ are calculated for each J , so as J increases higher l states are added, increasing NEVAL. At about $J = 28$, the lowest level with $l = 28$ is beyond the cutoff so no new states are added. Secondly, the energy of the rotationally excited states is roughly proportional to $J(J + 1)$. So as J increases all states increase in energy, this pushes some states beyond the $18\,000\text{ cm}^{-1}$ cutoff, reducing NEVAL. NEVAL peaks at $J = 15$ and declines steadily thereafter.

7.2.2 Problems Encountered.

The limiting factors on the rate at which the calculations can proceed are governed by the available computer resources. These are the main core memory or RAM, the number and speed of the processors and the available hard disk space.

During the course of the calculation the limiting factor proved to be the available disk

space. The disk space is primarily used to store the wavefunction files. The output from DVR3DRJZ take up $120(J+1)$ Mbytes. The scratch disk space available on miracle, is 100 Gbytes more than sufficient for the DVR3DRJZ output. However with roughly half the scratch disk in use by other users, problems arose with the wavefunctions output by ROTLEV3. These wavefunctions are about 15 Gbytes for each parity and each J . For the calculations between J and J' , four of these files need be stored. This requires a minimum disk space of 60 Gbytes, more than available. As a consequence 70 Gbytes of new disk space was fitted to miracle to allow the calculation to proceed. This still limits calculations to two J states at a time, there is simply not enough space to store wavefunctions for a third J . This imposes limits on the way in which the calculation can be done. The method in which the calculation was performed is as follows:

1. Calculate full wavefunction for state J .
2. Calculate full wavefunction for state $J' = J + 1$.
3. Calculate transitions between state J and J' .
4. Delete wavefunctions for J .
5. Begin calculation of wavefunctions for state $J'' = J' + 1$, calculate $e - f$ transitions for J' .
6. Set $J = J'$ and $J' = J''$ and return to step 3.

Other limitations were a result of the available RAM. The DIPOLE3 module requires by far the most memory. DIPOLE3 was effectively parallelised, see section 5.3.3, however the parallelisation is not very salable. As a consequence it proved to be most effective to run two calculations of DIPOLE3, on a reduced number of processors, simultaneously. Miracle has 4 Gbytes of RAM available for calculations. The largest DIPOLE3 calculations require over 2.3 Gbytes of RAM, consequently only one calculation could be performed at a time. Again slowing the rate of calculation.

A further problem was encountered for $J > 33$, this was a result in a bug in the DVR3DRJZ module which only manifested itself at high J . The problem lay in the routine JACOBI in DVR3DRJZ which determines the points and weights of the Gauss-Jacobi quadrature. For $J > 33$ the points and weights that were being determined were in error. The routine JACOBI was corrected, see section 5.3, and DVR3DRJZ ran correctly.

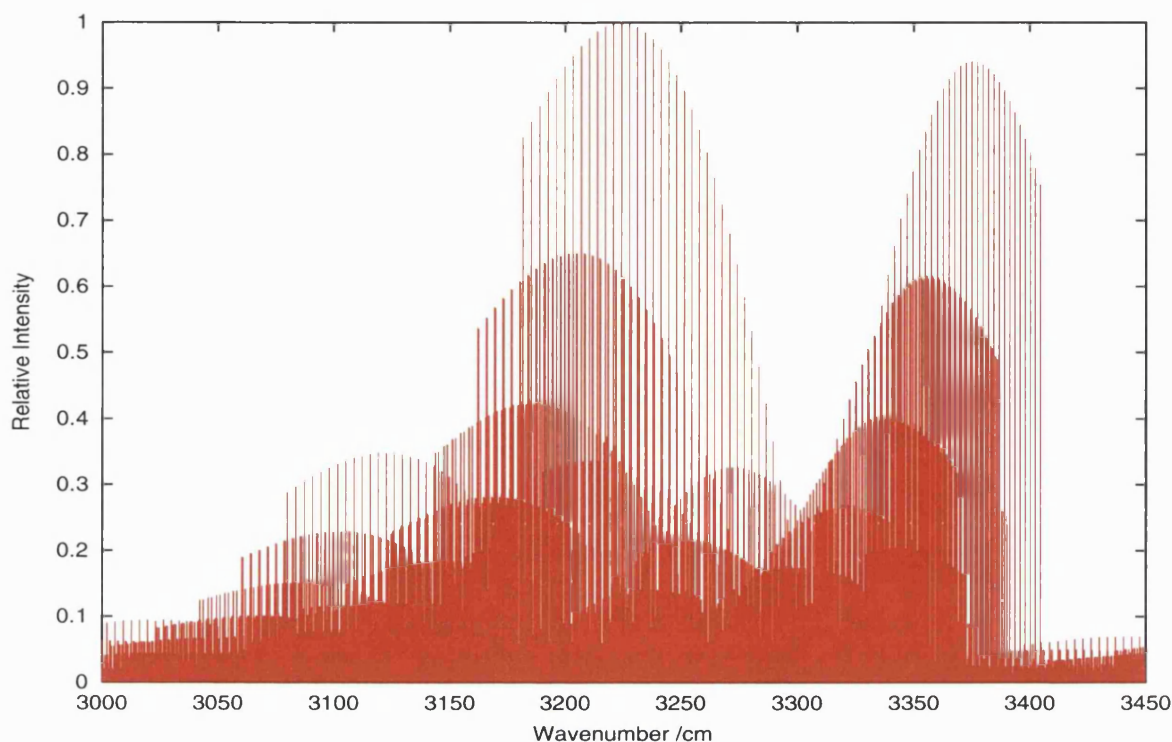


Figure 7.2: Stick absorption spectrum at $T = 2800$ K, in the region of the HCN C-H stretch fundamental. The spectrum includes lines with J up to 38 only.

7.3 The Linelist.

7.3.1 Present State of the Calculation.

At present (6/12/2001) the calculation is complete to $J = 38$ and extends up to 18 000 cm^{-1} above the zero point energy. The data calculated consists of over 125 000 energy levels and over 336 million line frequencies and transition dipole's.

Figure 7.2 shows a stick spectrum of the HCN (100) fundamental and its numerous hot bands at $T=2800$ K. Although the band peaks at $J \sim 26$, the truncation in J results in an abrupt end in the band profile. Clearly the cutoff at $J = 38$ is still to low and the calculation will need to be extended somewhat further.

7.4 Storage and Presentation of Data.

The linelist, consists of over 125 000 energy levels and over 336 million line frequencies and transition dipoles. This is quite simply a huge amount of data that needs a lot of storage space.

To fully describe each line, 6 integers and 4 floating point variables need to be stored. At 8 bytes per variable, this is 80 bytes per record. For 330 million records this is 24.5 Gbytes. This size of file is not easily manipulated or ported from machine to machine. Ideally we would like to reduce the overall size of the file and split it into smaller blocks of data which cover specific frequency ranges. The following discussion covers the compact method that has been chosen to store the data.

As mentioned to fully describe each line we require 6 integers and 4 floating point variables. The 6 integers are the quantum numbers of the upper and lower states: $J', p', n', J'', p'', n''$. Where J is the total angular momentum, p is the parity, and n refers to the n^{th} state in the J, p symmetry block. The four floating point variables are the energies of the upper and lower states (E', E''), the transition frequency (ω) and the transition probability (S). There are two facts that allow us to store the data in a more compact format. These are:

1. The ω can be calculated from E' and E'' .
2. The quantum numbers and energies of each energy level are repeated throughout the data file.

Consequently the full transition file can be split into an energy level file and a transition probability file. The quantum numbers and energies of each level are stored in the energy level file, each level is given a unique index integer. The index numbers of the upper and lower state and the transition probability are stored in the transition probability file. There are 4 integers and 1 floating point variable in the energy level file, corresponding to 40 bytes per level, for 125 000 levels this is 4.7 Mbytes. There are 2 integers and 1 floating point variable in the transition probability file corresponding to 24 bytes per transition and 7.4 Gbytes for 330 000 000 transitions. Clearly this is a more efficient way of storing the linelist resulting in nearly a factor of three reduction in file size. Short extracts from the energy level file and the transition probability file are given in tables 7.1 and 7.2.

A file size of 7.4 Gbytes is still too large to handle easily, further methods of reducing file size should be considered. It is often the case that only a small portion of the spectrum is of interest. It was therefore decided that the file be split into smaller files each with a specific frequency range. The frequency ranges were chosen so that if possible the strongest bands were not split over two files. The data was also sorted into frequency order. Finally

Table 7.1: An extract from the full energy level file.

index	J	p^a	n	$E \text{ (cm}^{-1}\text{)}^b$
30994	12	1	1604	1665.701511
30995	12	1	1605	1667.020228
30996	12	1	1606	1667.058702
30997	12	1	1607	1667.067369
30998	12	1	1608	1667.178129

^a If $p = 1$ this is an e state, if $p = 0$ this is an f state.

^b This is the energy of the level relative to the zero of the PES. The zero point energy is $3481.5053 \text{ cm}^{-1}$.

Table 7.2: An extract from the transition probability file, upper state is i lower state is j .

index i	index j	S_{ij}^a
125504	107907	0.398614E-08
118655	117196	0.325471E-19
71720	75513	0.851470E-09
30955	32798	0.782667E-08
44730	42594	0.617647E-14

^a This is $S(f - i)$ in Debye².

all transitions with a transition dipole of less than $1\text{e-}10$ Debye were excluded from the data. The permanent dipole of HCN is 2.96 Debye, as intensity is proportional to the square of the transition dipole the data spans over 20 orders of intensity magnitude.

Both the energy level file and the frequency ordered transition probability files can be retrieved via anonymous ftp ([ftp.tampa.phys.ucl.ac.uk](ftp://ftp.tampa.phys.ucl.ac.uk)) or via the Tampa group web page (www.tampa.phys.ucl.ac.uk). A compaction code is provided, which allows a choice of units.

7.5 An Opacity and Emmissivity Function For HCN/HNC.

In chapter 1 the importance of the absorption coefficient k_ν was discussed. In this section I present an integrated absorption coefficient which has been calculated from the linelist presented in the last section.

It was discussed in section 3.3 that the absorption coefficient of a line was related to its integrated absorption, S_i , by equation 3.38. We can extend this discussion to the

integrated absorption for the complete spectrum:

$$\begin{aligned} S &= \frac{1}{pl} \int_{-\infty}^{+\infty} \ln \left(\frac{I}{I_0} \right)_{\nu} d\nu \\ &= \sum_i S_i \end{aligned} \quad (7.1)$$

where S is the integrated absorption for the entire spectrum and S_i is the integrated absorption of line i . The integrated absorption of the spectrum (S) is of limited use. We wish to obtain k_{ν} the absorption coefficient at frequency or wavenumber ν . The absorption coefficient of the spectrum is given by:

$$k_{\nu} = \sum_i S_i f_i(\nu - \nu_{i0}) \quad (7.2)$$

where f_i is the line profile and ν_{i0} is the line center of line i . Clearly to calculate k_{ν} one would need to know the line profile of each line and be able to sum over all lines. k_{ν} may need to be determined at many frequencies and for over 3×10^8 lines this becomes impractical. Instead, here we assume each line is infinitesimally narrow, the line strengths in the region ν to $\nu + \Delta\nu$ are then summed and divided by $\Delta\nu$. This frequency binning method gives an approximate average value for k_{ν} in the region ν to $\nu + \Delta\nu$. It also has the effect of reducing the resolution of the full spectrum to $\nu/\Delta\nu$. Frequency binned opacity data has been presented by, for example, Schryber *et al* [176] and Neale *et al* [177].

To demonstrate the usefulness of our linelist we which to compare our opacity data with observed stellar spectra. The current near to mid infrared telescopes have a limited spectral resolution. For example the resolving power of ISO's SWS01 (speed) spectrometer is about 200 [175], this is the standard, but lowest resolution of SWS. At about 700 cm^{-1} this corresponds to a $\Delta\lambda$ of about 3 cm^{-1} . So for spectra of comparable resolution integrated absorption intensities have been put into bins of 3 cm^{-1} . Figure 7.3 shows the resulting absorption coefficient (k_{ν}) in the spectral region of 300 -1100 cm^{-1} at 3000 K. In this band there are over 61 million lines, the main features are a result of Δv_2 HCN and HNC bending fundamentals and hot bands, centred on 715 cm^{-1} and 465 cm^{-1} respectively. For comparison figure 7.4 shows a stick spectrum over the same spectral range and at the same temperature. Again the major features are the $\Delta v_2 = 1$ fundamental and hot bands of HCN and HNC. Also visible is the $\Delta v_2 = 2$ HNC bend overtone and hot bands centered on 920 cm^{-1} . It must be noted that in figure 7.3 STP is part of the unit system of $\text{cm}^{-1}\text{atm}^{-1}$. The units refer to the number density of a gas at STP. The number density in a real C-star atmosphere will be much less than in a gas at STP. Consequently,

to produce the same level of absorption, the path length in stellar atmospheres will be longer.

The absorption coefficient and integrated line absorption for the spectral range 1100 to 3900 cm^{-1} are shown in figures 7.5 and 7.6. In this region there are over 136 million lines and there are several strong absorption features. These are the HCN $\Delta v_2 = 2$ overtone and its hot bands at $\sim 1400 \text{ cm}^{-1}$, the HNC CN stretch fundamental and hot bands at $\sim 2000 \text{ cm}^{-1}$, the HCN $(10^00) - (01^10)$ band and its hot bands at $\sim 2600 \text{ cm}^{-1}$, the HCN HC stretch fundamental and hot bands at $\sim 3300 \text{ cm}^{-1}$ and finally the HNC HN stretch fundamental and hot bands at $\sim 3660 \text{ cm}^{-1}$. The HCN CN fundamental, its hot bands, the $\Delta v_2 = 3$ overtone and hot bands at $\sim 2100 \text{ cm}^{-1}$ are just discernable. As is the Q branch of the $(01^11) - (000)$ band at $\sim 2800 \text{ cm}^{-1}$. Again in this spectral range HNC features contribute significantly to the opacity and lie in regions where there is little HCN absorption.

We have used a HCN/HNC partition function of 25499.4 at $T=3000 \text{ K}$, which was calculated from the energy levels. This partition function is likely to be too low as it uses only levels with $J \leq 38$. At 3000 K levels beyond $J = 38$ are significantly populated, see section 7.3.1, and will contribute to the partition function. A more accurate partition function is being calculated by a collaborator as a work external to this thesis. An incorrect partition function will effect the absolute intensities and the absorption coefficient. Therefore when a better partition function is available the absolute intensities and absorption coefficient may need correcting.

To demonstrate how the opacity changes with temperature the absorption coefficient has been calculated at $T = 2800, 2300, 1800$ and 1200 K , each with a partition function calculated at the relevant temperature. The results are shown in figure 7.7. An increase in temperature has several effects. The HCN bending fundamental and hot bands, at 715 cm^{-1} , are dominant at all the shown temperatures. However as the temperature increases the band broadens as a result of higher populations in the high J states and in the excited vibrational states. The peak intensity, caused by the Q branch of the bending fundamental, drops because of the lower population of the ground state. At the same time the populations of the ground and excited HNC states increase with temperature so that the opacity caused by the HNC features at 400 to 600 cm^{-1} and 850 to 1100 cm^{-1} increase.

The linelist is currently truncated at $J = 38$. To determine the effect this truncation

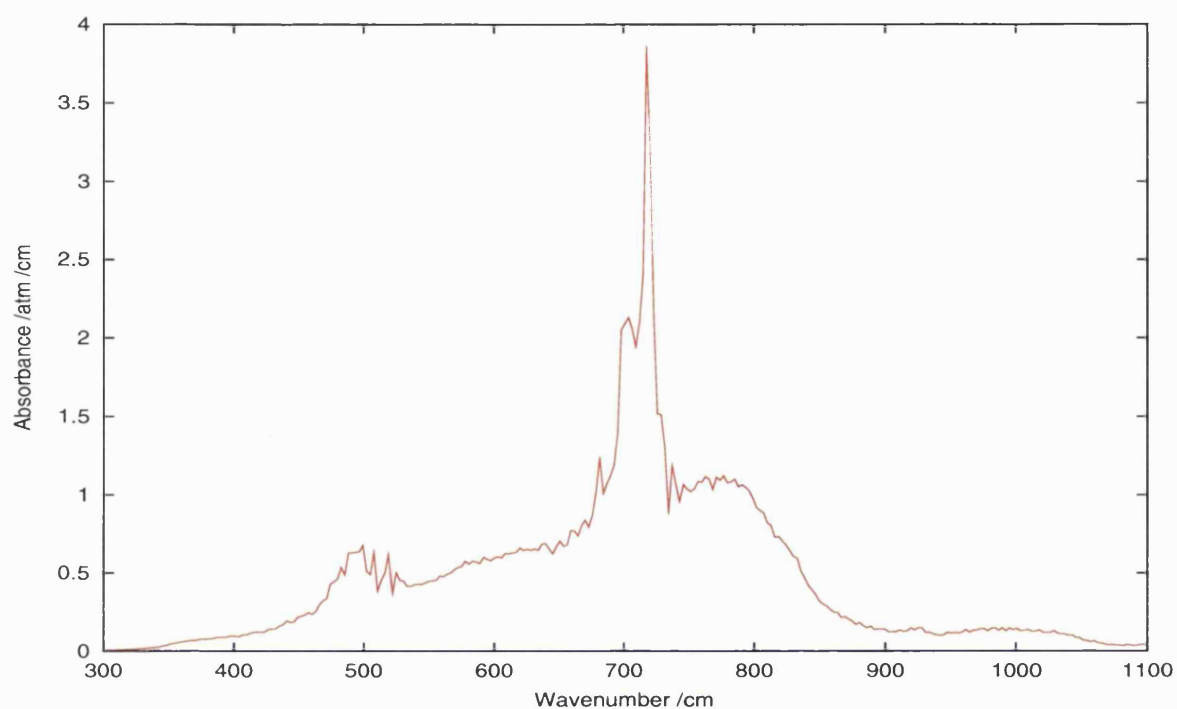


Figure 7.3: The absorption coefficient at $T = 3000$ K at STP, in the region of the HCN and HNC bend fundamentals.

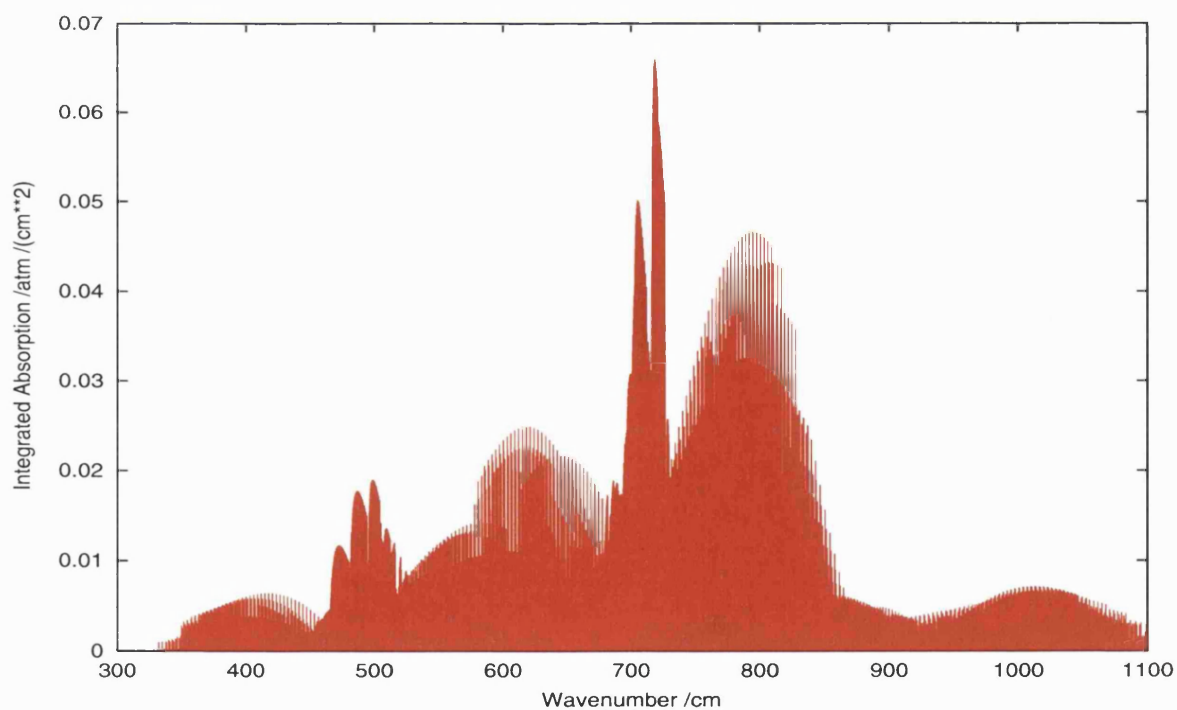


Figure 7.4: Integrated absorption at $T = 3000$ K at STP, in the region of the HCN and HNC bend fundamentals.

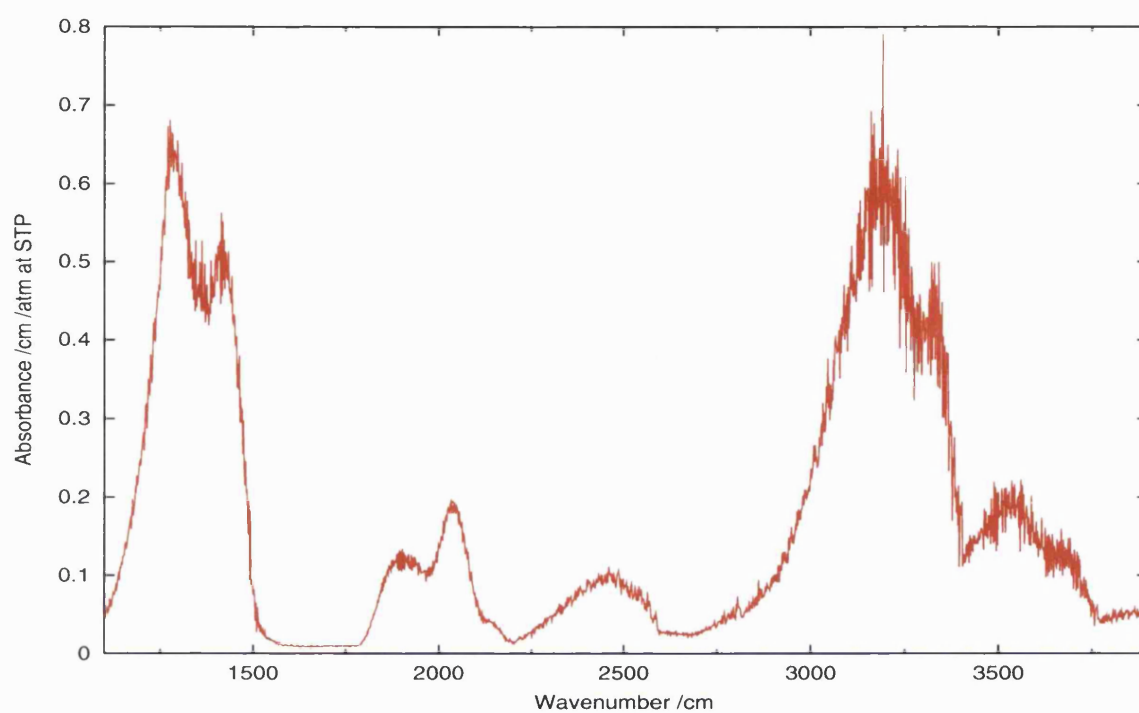


Figure 7.5: The absorption coefficient at $T = 3000$ K at STP, in the region of the HCN and HNC stretch fundamentals.

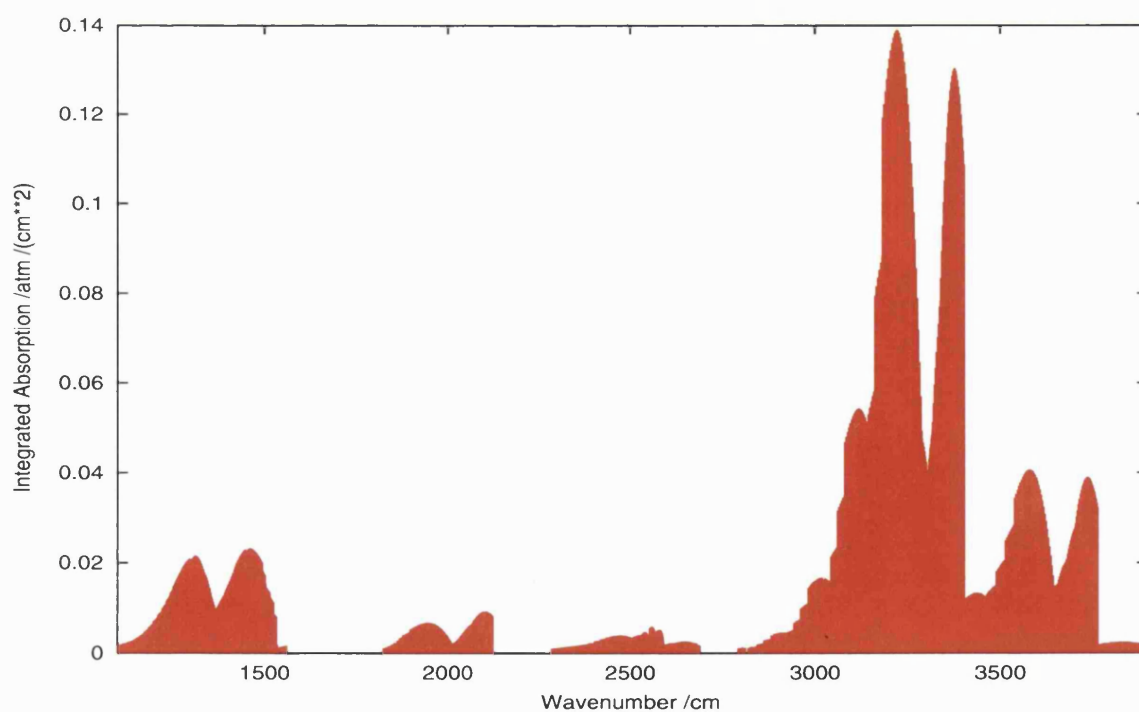


Figure 7.6: Integrated absorption at $T = 3000$ K at STP, in the region of the HCN and HNC stretch fundamentals.

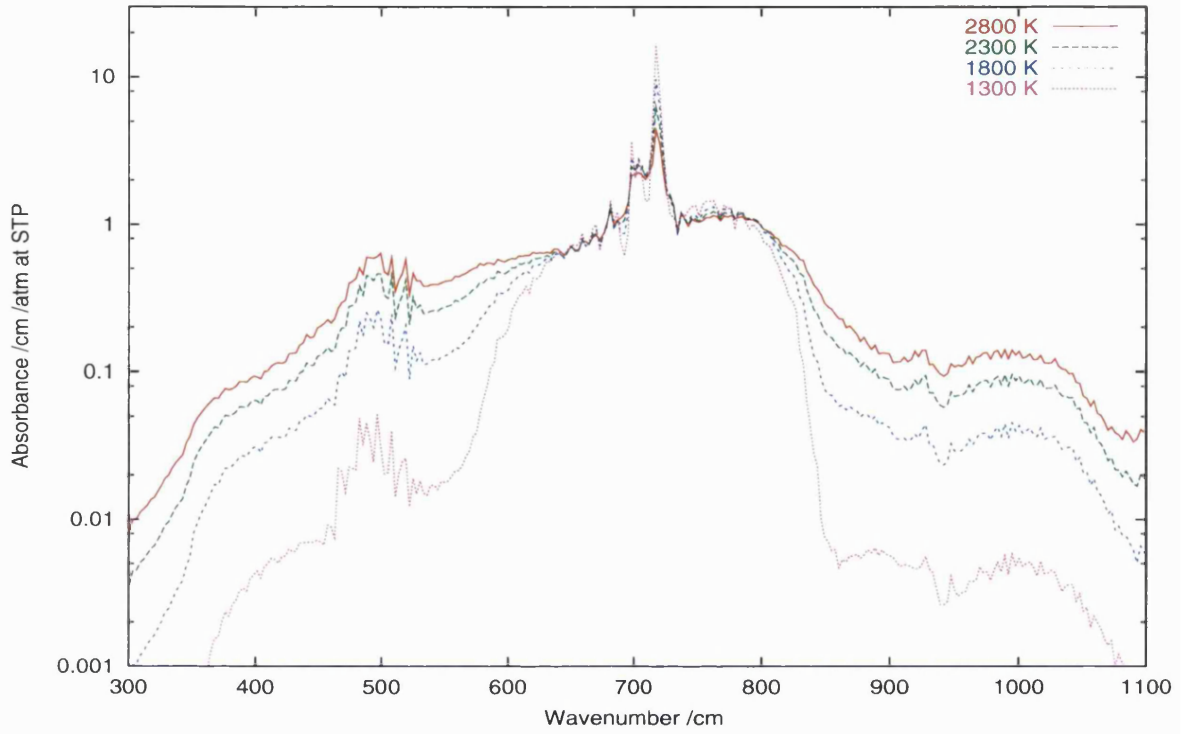


Figure 7.7: Integrated absorption at $T = 2800, 2300, 1800$ and 1300 K at STP, in the region of the HCN and HNC bend fundamentals.

has on the high temperature opacity function we have calculated the opacity function, at $T = 2800$ K with J truncated at $J = 38, J = 32, J = 28$ and $J = 23$. The resulting opacity functions are shown in figure 7.8. A value of 20253.6 for the partition function at 2800 K has been used. Clearly as J_{max} increases the opacity at every frequency increases and the absorption features broaden. This is primarily as result of the addition of more lines that involve a lower state which is significantly populated. If the addition of lines with a higher J_{max} made little or no difference to the opacity then lines with J_{max} would not need to be included. Unfortunately it appears that this stage has not yet been reached, although the difference between opacity curves appears to be diminishing as J_{max} increases.

7.6 High Temperature Absorption Spectra.

In this section I aim to calculate some simple absorption spectra for comparison with observation. To generate some simple absorption spectra we consider beam of intensity I_λ passing through a gas of uniform composition of HCN/HNC at temperature T . We assume that the emission from the gas is negligible so that the intensity of the beam is given by

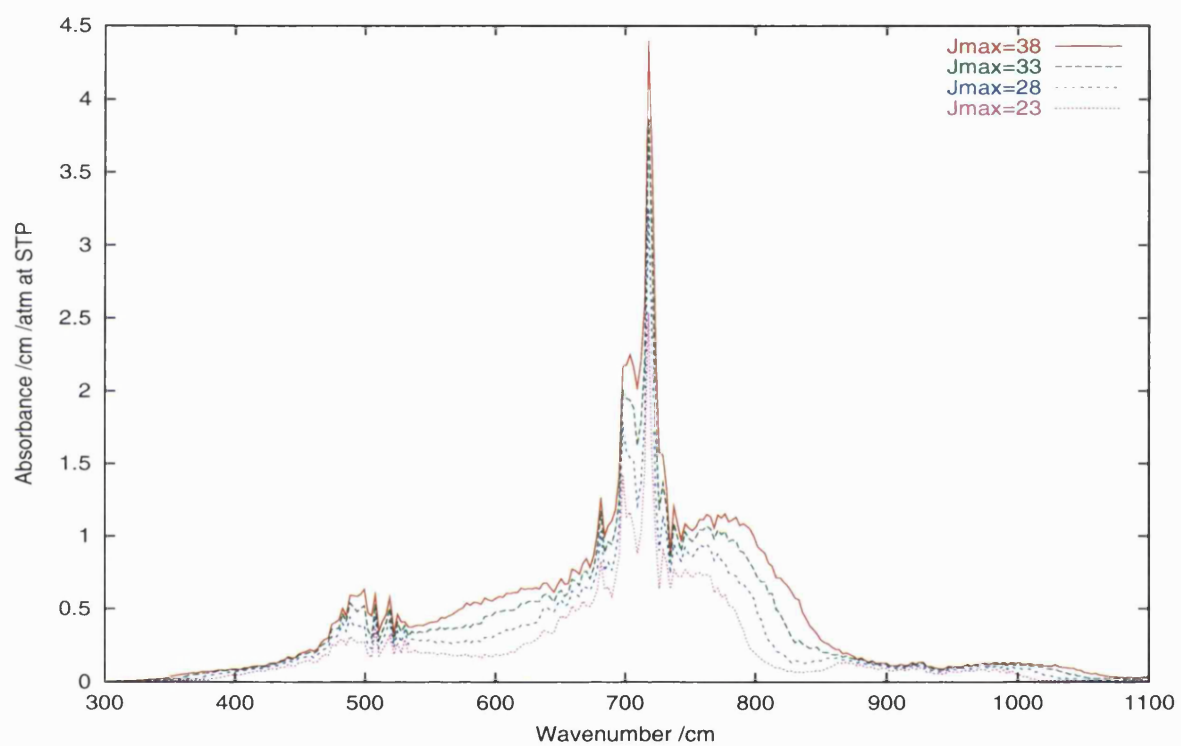


Figure 7.8: Integrated absorption at $T = 2800$ K at STP with J truncated at values of 38, 33, 28 and 23. The wavenumber range selected is in the region of the HCN and HNC bend fundamentals.

the Lambert-Beer law, equation 3.37. This allows a determination of the transmittance (I/I_0) of the beam, from κ_ν .

The observed stellar spectra of Aoki *et al* [16, 52] are given in wavelength units. However, up until now the calculation has been in wavenumber units, so the units need to be changed to wavelength units. The opacity or absorption coefficient given here is a function of wavenumber or wavelength, however it is independent of wavenumber units. So the opacity is not affected by the change from wavenumber to wavelength.

The spectrum in the region 2.8 to 8 μm is shown in figure 7.9. This is the same range as the ISO-SWS spectra of 6 C-stars taken by Aoki *et al* [16], see fig. 7.10. The three lower spectra in figure 7.10 are of C-stars that contain HCN and the upper three spectra are of stars in which HCN is not known to be present. Most of the main features in the HCN/HNC spectra (fig 7.9) appear to correlate well with the stellar spectra. For example the 3.2 μm , 4 μm and the 7-8 μm features are present in both HCN/HNC and stellar spectra. The ~ 5 μm HNC CN stretch feature present in the HCN/HNC spectrum, may also be present in the stellar spectra. However this is difficult to tell as is likely to be absorption from other molecular species in this region, possibly C_3 [16].

The spectrum over the range 9 to 30 μm , is shown in figure 7.11. This can be compared to figure 1.2 which shows the ISO-SWS spectra of four C-stars, in the region 7-20 μm , taken by Aoki *et al* [52]. The most striking features are the Q branches of the HCN bending fundamental at ~ 14 μm . Also visible are the Q branches of the HNC bending fundamental and hot bands at ~ 20 μm . This hints that HNC is an important opacity source in C-star atmospheres and may be detectable at around 20 μm . This is on the edge of the C-star spectra in figure 1.2 so impossible to see in these spectra. In fact most of the absorption immediately to either side of the HCN bending fundamental and its hot bands is a result of HNC absorption.

Aoki *et al* [16] took high resolution spectra of TX-Psc and WZ Cas in the 2.75 to 4.2 μm region. They used ISO's SWS06 spectrometer, which has a resolution of around 1500 [52]. Figure 7.12 shows the spectrum of TX Psc and WZ Cas taken by Aoki *et al* [16] the model atmospheres fitted by Aoki *et al* are also shown. WZ Cas shows strong HCN features whereas in TX Psc the HCN features are much weaker [16, 52]. For comparison with these stellar spectra we have calculated a HCN/HNC spectrum in the same region, see figure 7.13. Again the 2 major features, at 3.2 μm and 4 μm of the spectrum of WZ Cas are present in the HCN/HNC spectra. In fact as regards the 4 μm feature is concerned

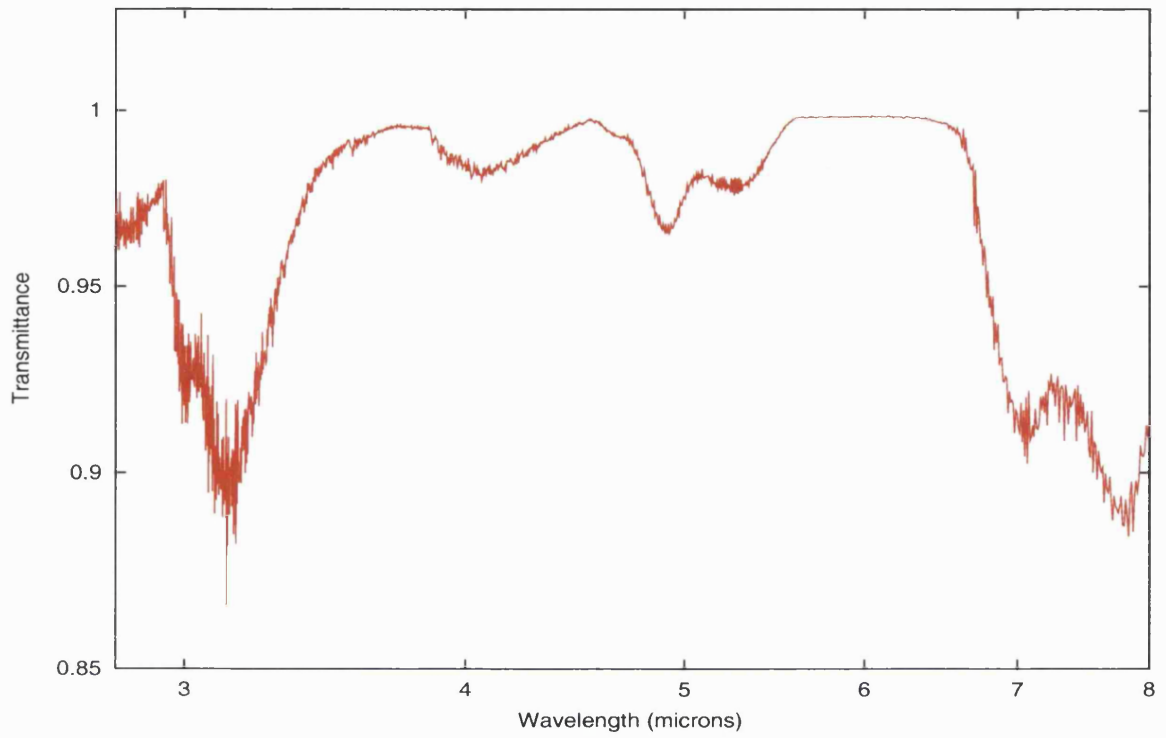


Figure 7.9: $\frac{I}{I_0}$ using a path length of 2 cm at 1 atmosphere at $T = 3000$ K. The wavenumber range selected is in the region of the HCN and HNC stretching fundamentals and the $\Delta v_2 = 2$ overtone. The resolution is $\sim 0.002 \mu\text{m}$

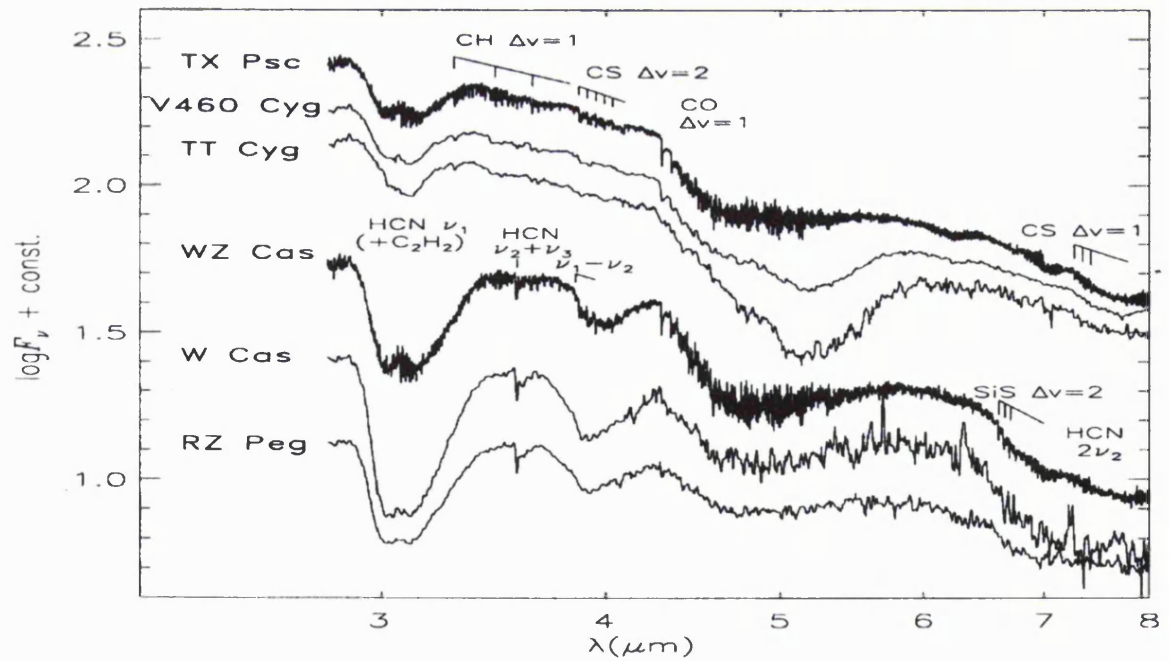


Figure 7.10: ISO SWS spectra of 6 carbon stars in the region 3-8 μm . Taken from Aoki *et al* [16].

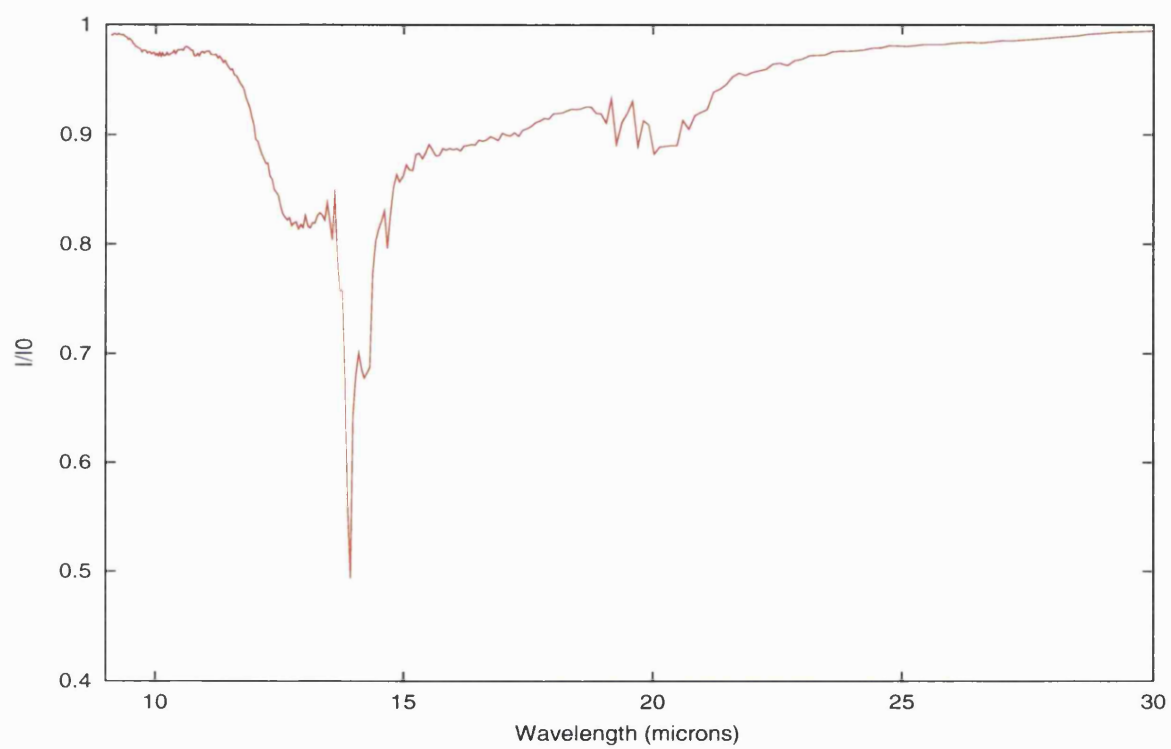


Figure 7.11: $\frac{I}{I_0}$ using a path length of 2 cm at 1 atmosphere at $T = 3000$ K. The wavenumber range selected is in the region of the HCN and HNC bend fundamentals. The resolution is $\sim 0.06 \mu\text{m}$

the HCN/HNC spectrum appear to correlate more closely to the observed spectrum than do the model atmospheres of Aoki *et al* (solid lines in fig. 7.12). The $4\ \mu\text{m}$ feature is attributable to the $(10^00) - (01^10)$ band and its hot bands. The limited nature of the HCN spectroscopic data of Aoki *et al* [16] included transitions with bend excitations upto $v_2 = 4$. To try to better model this feature Aoki *et al* [16] used an empirical extension to their data to extend it upto $v_2 = 9$. The spectra from the model atmosphere at 2800 K, calculated by Aoki *et al* [16], using their extended HCN data is shown in fig. 7.12 (dotted line). This model atmosphere compares considerably better with the spectrum of WZ Cas and our HCN/HNC spectrum. Clearly the higher vibrational levels are of significance to the opacity of the stellar atmosphere. Aoki *et al* [16] identified the Q branch of the $(01^11) - (00^00)$ overtone in the spectrum of WZ Cas. The Q branch of this band is just visible in the HCN/HNC spectrum at $\sim 3.55\ \mu\text{m}$, but is much less pronounced than in the model atmosphere spectra of Aoki *et al* [16]. The $\sim 2.85\ \mu\text{m}$ HNC HN stretch feature present in the HCN/HNC spectrum is perhaps visible in the spectrum of WZ Cas. It is however difficult to confirm as this region is on the edge of the stellar spectra. However this region may be the region of the spectrum in which HNC could be most readily looked for. It does not have the problems of the HNC CN stretch mode at $5\ \mu\text{m}$ which is in a region in which there is a lot of absorption from other molecular species.

Aoki *et al* [52], in ISO SWS06 observations around $14\ \mu\text{m}$ detected HCN in emission and absorption. The emission is believed to come from a shell of cool gas around the star. Figure 7.14 shows the observed spectrum of TX Psc, the fitted model atmosphere and 500 K emission spectra of Aoki *et al* [52]. The absorption of the $14\ \mu\text{m}$ Q branches in the stellar spectrum in figure 7.14 is almost completely canceled out by emission. For comparison with both the stellar and model spectra of Aoki *et al* [52], we have calculated a HCN/HNC absorption spectrum in this region, see figure 7.15. In general the features in the HCN/HNC absorption spectrum compare well with the main features of model atmosphere. However in the region ~ 14 to $14.4\ \mu\text{m}$ there is considerably more absorption in the spectrum calculated in this work than there is in the model atmosphere of Aoki *et al* [52]. This is likely to be a result of the limited $\Delta v_2 = 1$ data used by Aoki *et al* [52], which consists of energy levels with $v_2 \leq 4$ and $v_3 \leq 1$. The data calculated in this work is considerably more extended than the relatively small sample, used by Aoki *et al* [52]. The HCN/HNC spectrum shown in figure 7.15, appears to have a significant amount of noise, especially at the lower wavelengths. This however is not noise but the result of

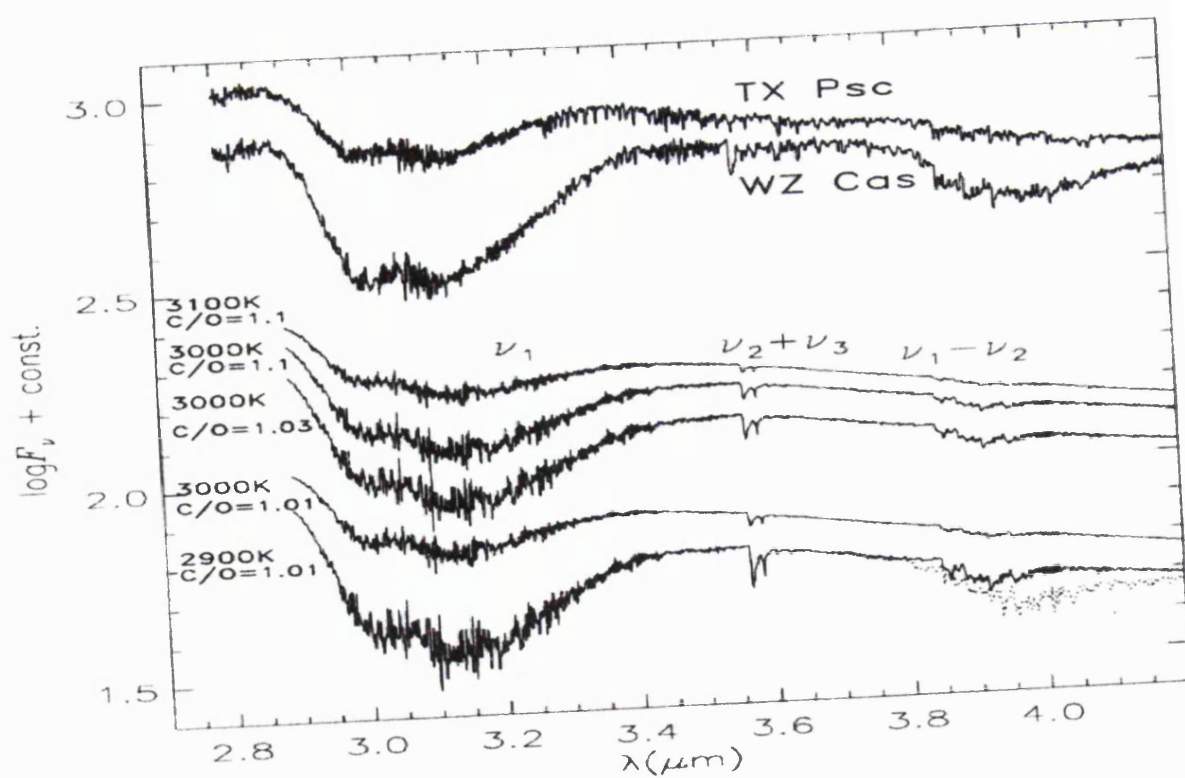


Figure 7.12: Spectrum of TX Psc and WZ Cas (upper two), with the synthetic spectra (lower 5). Taken from Aoki *et al* [16].

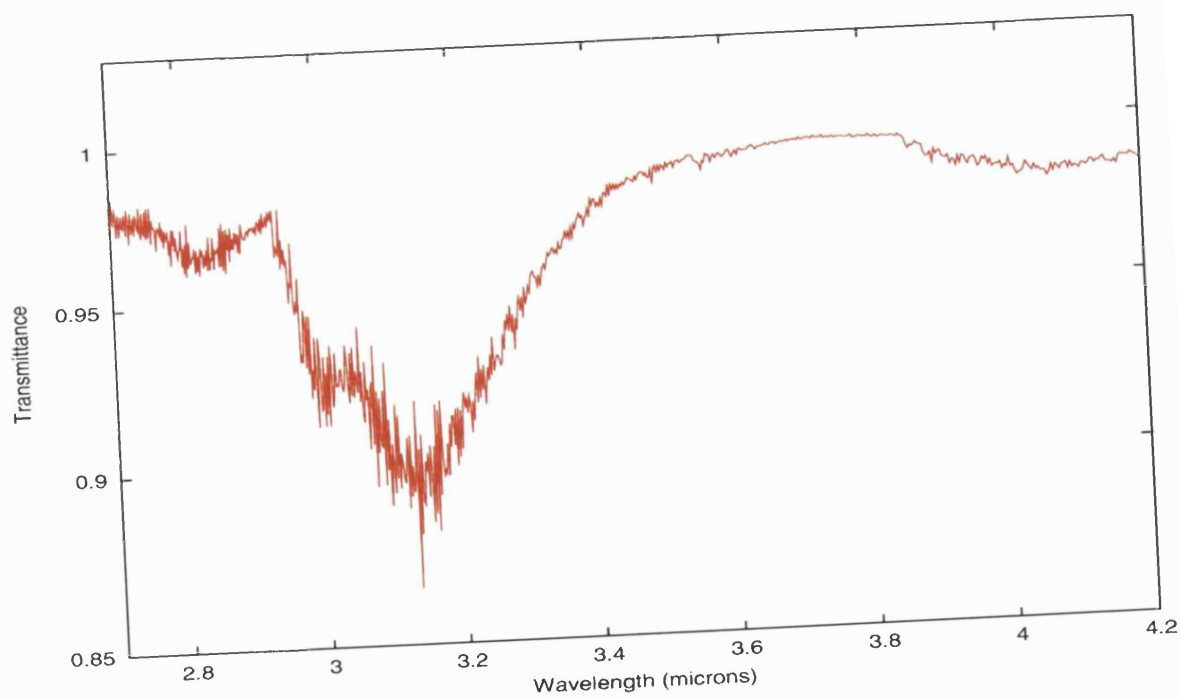


Figure 7.13: $\frac{I}{I_0}$ using a path length of 2 cm at 1 atmosphere at $T = 3000$ K. The resolution is $\sim 0.002 \mu\text{m}$

absorption by real lines of the $\Delta v_2 = 1$ bands.

7.7 Conclusion and Further Work.

7.7.1 The New *ab initio* Surfaces.

In chapter 4 new *ab initio* PES, DMS, DBOC and relativistic correction surfaces were presented.

The *ab initio* VQZANO+ PES is a fit to both the *ab initio* electronic potential energy calculations of my collaborator van Mourik, and of Bowman *et al* [116]. Van Mourik's calculations were performed at the CCSD(T)/cc-pCVQZ level. Where as those of Bowman *et al* [116] also used CCSD(T) and were more extensive, but a smaller ANO type basis set was used. The PES is morphed using 17 *ab initio* aug-cc-pCVQZ points calculated at the HNC end of the PES. This morphing improves the representation of the HNC region of the potential, and reduces the error of the calculated band origin of the HNC H-N stretch fundamental. The 3 critical points of the surface were remapped to high accuracy *ab initio* cc-pCV5Z electronic potential points optimised to lie at the critical points. This improved the geometry of the PES, so that the error on the rotational levels calculated with the PES was reduced.

The new *ab initio* DMS is a fit to the electronic structure calculations of van Mourik performed at the CCSD(T)/cc-pCVQZ level. The new *ab initio* DBOC and relativistic correction surfaces are fits to the *ab initio* calculations of Császár, see chapter 4.

The new *ab initio* PES, DMS, DBOC and relativistic correction surfaces presented in this work are fitted to the best available electronic structure data. As a result, for energies below 25 000 cm^{-1} these surfaces are the best currently available.

7.7.2 The Preliminary Calculations.

In chapter 5 preliminary $J = 0$ vibrational band origins, rotational levels and some band transition dipoles were calculated. In general the vibrational band origins calculated with the new VQZANO+ PES compare more closely with experiment than do the band origins calculated with the Bowman *et al* [116] PES. The rotational energy levels calculated with the VQZANO+ PES compare an order of magnitude more closely with experiment than those calculated with the PES of Bowman *et al* [116]. The band transition dipole's calculated with the μ QZ DMS of this work agree more closely with experiment than do

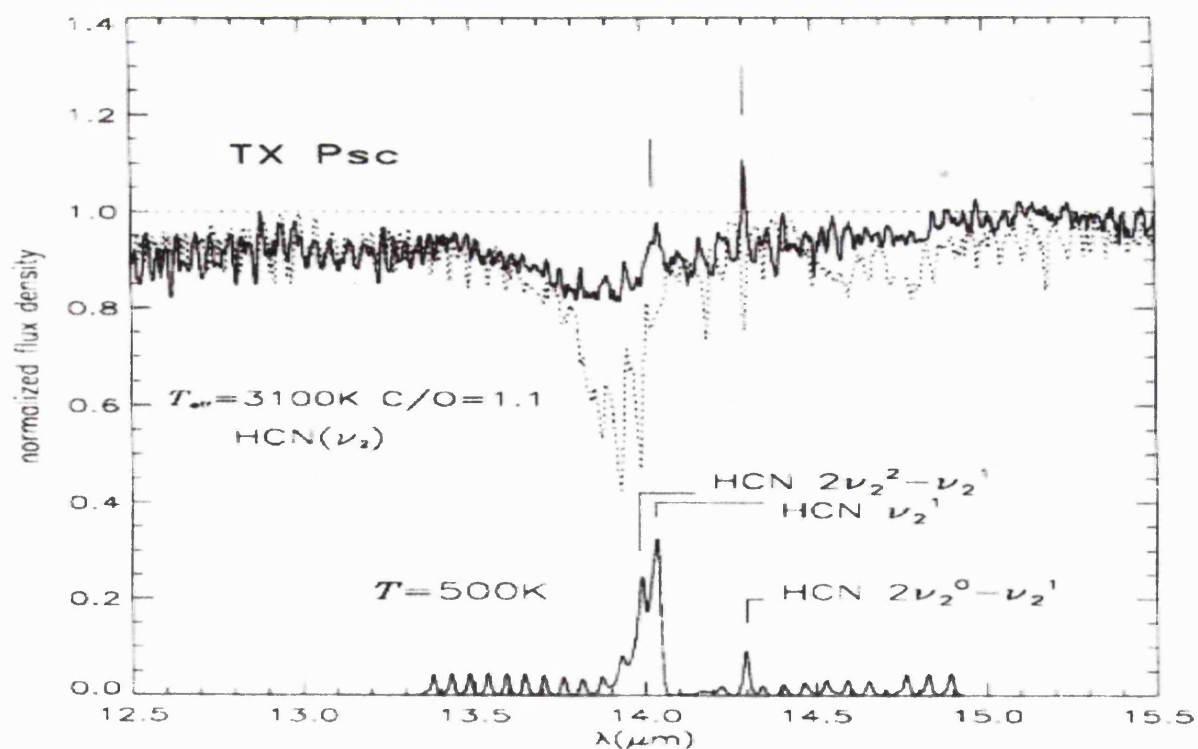


Figure 7.14: Spectrum of TX Psc (solid line), with synthetic spectra (dotted line) and 500 K HCN emission. Taken from Aoki *et al* [52].

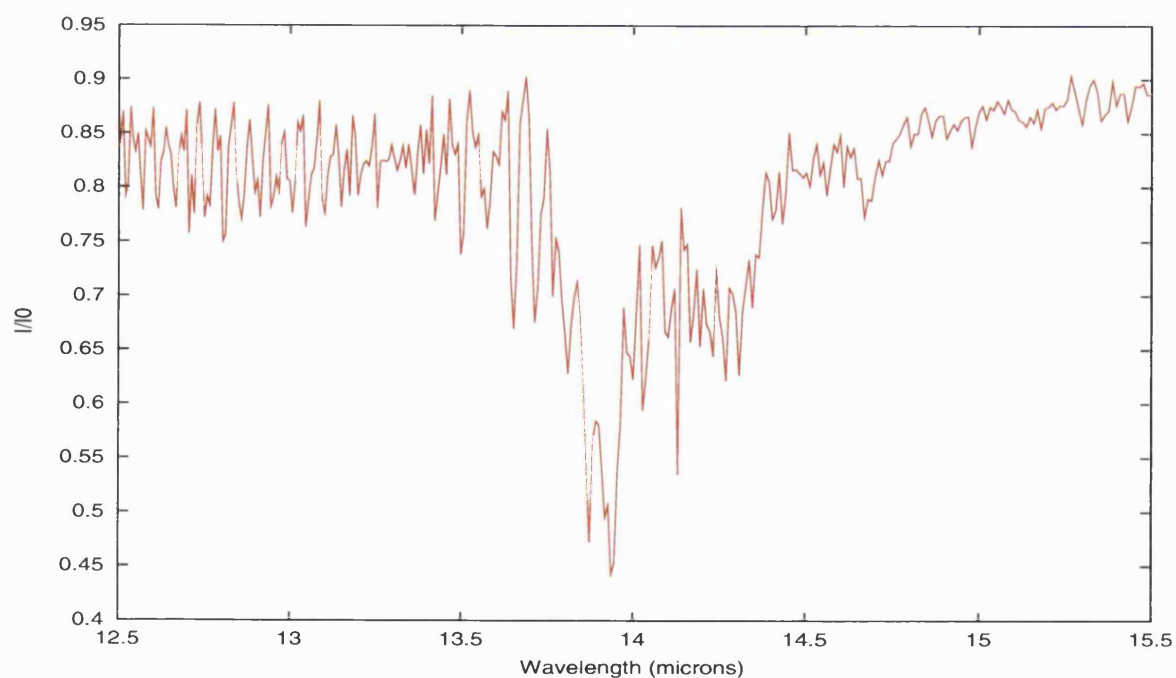


Figure 7.15: I/I_0 using a path length of 2 cm at 1 atmosphere at $T = 3000$ K. The resolution is $\sim 0.01 \mu\text{m}$

those of any other 3D DMS.

7.7.3 Room Temperature Spectra.

In chapter 6 an extensive list of HCN and HNC band transition dipoles were calculated and room temperature absorption spectra were presented. In general the band transition dipoles agree more closely with experiment than do those of all previous 3D calculations. Room temperature spectral maps over the region $0\text{--}18\,000\text{ cm}^{-1}$ for HCN and over the region $0\text{--}8000\text{ cm}^{-1}$ for HNC, have been given.

The calculated integrated absorption intensities of the HCN forbidden $(02^20) - (00^00)$ band and the HCN $(00^01) - (00^00)$ fundamental band, agree well with experiment. Intensities for many bands which have not been previously reported were also presented.

7.7.4 The Linelist.

In this chapter the linelist was presented. Using the linelist a high temperature HCN/HNC opacity function was calculated and high temperature HCN/HNC absorption spectra were calculated. These spectra were then qualitatively compared with some real C-star spectra. The agreement between stellar spectra and *ab initio* HCN/HNC spectra appeared good, showing the usefulness of this new HCN/HNC linelist. It was also shown that if HCN and HNC are in thermodynamic equilibrium, HNC will play a significant role in the opacity of HCN containing C-stars. Possible regions in which HNC might be detected in C-stars has been identified as the regions of the HNC fundamentals at $\sim 2.8\text{ }\mu\text{m}$, $\sim 5\text{ }\mu\text{m}$ and $\sim 20\text{ }\mu\text{m}$. The hot bands of the $(10^00) - (01^10)$ band calculated in this work, that extend beyond the linelist of Aoki *et al* [16], were also shown to have a significant role in the opacity.

The HCN/HNC linelist discussed in this chapter extends only to $J = 38$. It was discussed that this cut-off in J was too low. The data in the final linelist will extend to $J=60$.

At present this linelist is the most extensive HCN/HNC data set in existence. The linelist is more accurate and more extensive than the *ab initio* HCN opacity data of Jørgensen *et al* [54], see section 1.4, that is used in the recent model C-star atmospheres of Loidl *et al* [55]. It is considerably more extensive than the data of Aoki *et al* [16], which is based upon experimental data, see section 1.4.

The linelist calculated here has not yet been used in full model atmospheres, only simple absorption spectra have been calculated. Only once the data presented here is used in

model C-star atmospheres can we determine the extent to which this linelist improves our understanding of C-stars and enable a re-evaluation of Jørgensens claim [54]. The linelist may well also have uses at lower temperatures (< 1500 K) in the modeling of proto-stellar objects, cometary comae and planetary atmospheres.

I would like this data to be used in the modeling of C-star atmospheres and elsewhere. The linelist will be made publicly available for this purpose.

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